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# THE BLEACHING, DYEING, AND CHEMICAL TECHNOLOGY OF TEXTILE FIBRES

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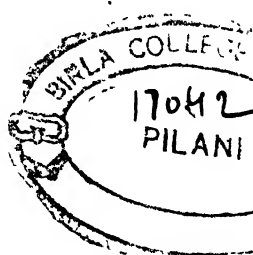
E. R. TROTMAN, M.Sc., Ph.D., F.R.I.C.

JOINT AUTHOR OF "ARTIFICIAL SILKS" AND "TEXTILE ANALYSIS"

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## PREFACE TO FIRST EDITION.

THIS book is based upon courses of lectures given in University College, Nottingham. It is intended, primarily, for students. For this reason the subject is treated, as far as possible, from a scientific rather than a purely utilitarian point of view. While many descriptions of processes are given, they are typical rather than exhaustive. Laboratory work in Textile Technology is designed also to teach "principles." The details of handling goods in bulk should be learnt by actual experience in a works. Although the book is suitable for a first, as opposed to a post-graduate course, full references have been made to the work of others, in order to encourage the student from the beginning to verify facts for himself, and to impress upon him the importance of wide and intelligent reading. With this object in view, much use has been made of readily available scientific journals, such as those of the Society of Chemical Industry and the Society of Dyers and Colourists. It is much better for a student to be able to find an abstract of a paper published in a foreign journal than to be referred to the original publication which is, in most cases, unobtainable.

Chemical compounds have been described as the knowledge of them becomes important. For example, the necessity for understanding the difference between amino and imino groups arises first when dealing with the constitution of keratin of wool. Hence, although the amines are mentioned earlier, their chief reactions are explained in connection with wool. Other amines, which are of interest chiefly as "developers," are described in the chapter dealing with developed and similar colours. The advantage of this method is that it enables the student to get on with the technology at the same time as he revises the chemistry, which is inseparable from it.

The analytical methods given for the testing of chemicals, dyestuffs, and textile materials are those which could be subsequently carried out by the student in a works. Processes which could be handled only by a skilled analyst have been omitted.

Practically all of the microphotographs used as illustrations were prepared by Mr R. W. Sutton, B.Sc., A.I.C., in the Authors' laboratory. In a few cases they were made from sections obtained from Mr A. Flatters of Bramhall.

S. R. T.  
E. R. T.

NOTTINGHAM,  
*February 1924.*

## PREFACE TO SECOND EDITION.

THE exhaustion of the first edition of this book has shown that it has taken a place in the literature of Textile Technology. The preparation of the second edition has been delayed by war conditions, but it is hoped that the information given of recent work will increase the usefulness of the book to students and others engaged in the textile industry.

S. R. T.  
E. R. T.

NOTTINGHAM,  
*November 1945.*



# CONTENTS.

## CHAPTER I.

	PAGES
The History of Dyeing—Preparation of Dyestuffs—Intermediates—Amines— Sulphonic Acids—Colour—Chromophores—Auxochromes . . . . .	1-9

## CHAPTER II.

Commercial Dyestuffs: Nomenclature—Classification—General Conditions of Dyeing . . . . .	10-12
---	-------

## CHAPTER III.

Ionization—Hydrogen-ion Concentration and pH-Values—Buffered Solutions —Indicators—pH-Meters—The Microscope—Colour Measurement . . . . .	13-31
---	-------

## CHAPTER IV.

Micro-organisms—Moulds—Yeasts—Antiseptics—Enzymes—Colloids . . . . .	32-41
--	-------

## CHAPTER V.

Theories of Dyeing . . . . .	42-46
------------------------------	-------

## CHAPTER VI.

Water: Classification—Impurities—Temporary and Permanent Hardness— Scale-forming Waters—Corrosive Waters—Foaming Waters—Water-softening— Permutit Process—Use of Sodium Hexametaphosphate and Barium Salts in Softening—Treatment of Water containing Organic Matter . . . . .	47-62
---	-------

## CHAPTER VII.

General Properties of Textile Fibres—Classification—Special Tests for Different Fibres . . . . .	63-66
---	-------

## CHAPTER VIII.

Physical and Chemical Tests for Textile Fibres—Relative Humidity of the Atmosphere—Moisture Content of Different Fibres—Regain—Determination of Condition, Count, Length, Tensile Strength, Twist, and Elasticity—Wear-testers —Analysis of Textile Materials . . . . .	67-89
--	-------

## CHAPTER IX.

Cotton: Natural History of Cotton—Spinning—Types of Commercial Cotton— Structure of Fibre—Constituents of Cotton—Cotton Oils and Waxes—Nitrogenous Constituents—Colouring-matters, Pectoses and Pectins, Mineral Constituents— Cellulose—Hydrocellulose—Oxycellulose—Cellulose Peroxide—Tannic Acid . . . . .	90-109
--	--------



## CHAPTER X.

PAGES

Special Properties of Cotton Cellulose—Action of Air, Water, Micro-organisms, Acids, Alkalis—Mercerized Cotton—Schreinerized Cotton—Immunized Cotton— Amidated Cotton . . . . .	110-121
---	---------

## CHAPTER XI.

Multicellular Vegetable Fibres—Flax—Ramie—Hemp—Jute . . . . .	122-128
---	---------

## CHAPTER XII.

Artificial Fibres—Nitro Rayon—Cuprammonium Rayon—Viscose Rayon— Staple Fibres—Cellulose-acetate Rayon—Casein Fibres . . . . .	129-138
--	---------

## CHAPTER XIII.

Silk: Sericulture—Microscopic Structure—Composition—Definitions—Prop- erties of Silk—Sericin—Fibroin—Action of Heat, Water, Light, Acids, Alkalis, Salts—Detection of Damage—Weighting of Silk—Wild Silk—Spider Silk . . . . .	139-152
--	---------

## CHAPTER XIV.

Wool and Hair: Structure of Skin—Varieties and Characteristics of Wool— Classification of Wool—Wool-sorting—Abnormal Fibres—Composition of Raw Wool—Keratin—Cystine—Properties of Wool—Felting—Action of Air, Heat, Light, Acids—Detection of Damage—Carbonization of Wool—Action of Alkalis, Soap, Bleaching Agents, Micro-organisms, Chlorine—Chlorination of Wool— Estimation of Damaged Fibres—Tests for Shrinkage . . . . .	153-189
---	---------

## CHAPTER XV.

Oils, Fats, and Waxes—Fatty Acids—Rancidity—Soaps—Emulsifying Power —Detergent Action—Rosin Soaps—Sulphonated Oils and Soaps—Types of Soap —Wetting Agents—Waterproofing Agents . . . . .	190-206
---	---------

## CHAPTER XVI.

Acids and Alkalis: Sodium Hydroxide—Potassium Hydroxide—Sodium Carbonate—Sodium Bicarbonate—Sodium Silicates—Borax—Ammonia—Sul- phuric Acid—Hydrochloric Acid—Formic Acid—Acetic Acid—Oxalic Acid— Tartaric Acid . . . . .	207-215
---	---------

## CHAPTER XVII.

Bleaching Agents: Sulphur Dioxide—Sodium Sulphite—Sodium Bisulphite— Sodium Hydrosulphite—Chlorine—Aqua Regia—Hypochlorous Acid—Eau de Javelle—Sodium Hypochlorite—Bleaching Powder: Properties, Analysis and Uses . . . . .	216-233
---	---------

## CHAPTER XVIII.

Non-chlorinated Oxidizing Bleaching Agents—Hydrogen Peroxide—Sodium Peroxide—Perborates—Persulphates—Potassium Permanganate—Potassium Di- chromate—Air as Bleaching Agent—Ozone . . . . .	234-245
---	---------

## CHAPTER XIX.

Organic Solvents: Petroleum Spirit—Benzene—Carbon Tetrachloride—Other Chlorinated Hydrocarbons—Hydrogenated Hydrocarbons and Phenols . . . . .	246-249
---	---------

## CHAPTER XX.

PAGES

Scouring and Bleaching of Silk: Boiling-off—Souple, Écru, and Chappe Silk— Loss on Boiling-off—Bleaching with Sulphur Dioxide, Hydrogen Peroxide, Sodium Peroxide, Potassium Permanganate—Bleaching of Souple Silk—Bleaching Tussur and Wild Silks . . . . .	250-261
---	---------

## CHAPTER XXI.

Scouring and Bleaching of Wool: Solvent Process—Emulsification Process— Removal of Oil—Removal of Calcium and Magnesium Soaps—Recovery of Waste Products—Analysis of Scoured Wool—Lubricating Oils for Wool—Bleaching with Sulphur Dioxide, Hydrogen Peroxide, Sodium Peroxide, Potassium Permanganate —Finishing of Woollen Goods—Turning—Fulling—Pressing—Nap-raising—Crab- bing—Decatizing . . . . .	262-284
--	---------

## CHAPTER XXII.

Scouring and Bleaching of Cotton: General Outline of the Process—Preliminary Operations—Lye Boiling—Keirs—The Caustic-soda Boil—The Lime Boil—Effects of Lye Boiling—Use of Organic Solvents—Bleaching or Chemicking—General Conditions affecting Bleaching, Souring, and Soaping—Bleaching with Sodium Hypochlorite, Hypochlorous Acid, Chlorine Water, Hydrogen Peroxide, Potassium Permanganate—Bleaching Coloured Goods—Testing Bleached Cotton—Damage and Defects due to Bleaching . . . . .	285-307
---	---------

## CHAPTER XXIII.

Cotton Finishing: Drying—Pure and Assisted Finishes—Beetling—Calendering —Yarn Finishing—Stiffening and Binding Agents—Starch—Dextrin—Glue and Gelatin—Algin—Gums—Irish Moss—Iceland Moss—Carnaúba Wax—Filling Materials—Softening Agents—Antiseptics—Blueing Materials—Fireproofing Agents—Application of Finishing Mixtures—Stentering . . . . .	308-336
--	---------

## CHAPTER XXIV.

Dyeing Machinery: Requirements—Materials used in Construction—Machines for Dyeing Yarn—Fabric-dyeing Machines—Footwear and Garment-dyeing Machines—Dyeing Jigger . . . . .	337-348
--	---------

## CHAPTER XXV.

Acid Dyestuffs: Nature and General Properties—Assistants—Function of Acid —Glauber Salt—Subdivisions of Acid Dyestuffs—Fastness of Acid Dyes—Applica- tion to Wool—Levelling Uneven Shades—Stripping Agents—Acid Chrome Dye- stuffs—Metachrome Colours—Neolan Dyestuffs—Application to Silk and to Cotton—Tests for Fastness of Dyestuffs . . . . .	349-367
---	---------

## CHAPTER XXVI.

Basic Dyestuffs: Chemical Nature and Classification—General Properties and Theories of Dyeing—Assistants—Application to Silk, Wool, and Cotton—Mordant- ing with Tannic Acid, Katanol, Fatty Acids, Direct Dyes . . . . .	368-380
---	---------

## CHAPTER XXVII.

Substantive or Direct Dyestuffs: Chemical Nature and Theory of Dyeing— Assistants—Factors affecting Dyeing—Application to Cotton, Wool and Silk . . . . .	381-390
--	---------

## CHAPTER XXVIII.

PAGES

Developed and Coupled Colours: Developers—Diazotization—The Coupling Bath—Naphthol or Insoluble Azoic Colours—"Para Red"—Other Azoic Colours—Naphthol-AS Colours—Azoic Colours on Wool and Silk or Union Goods . . .	391-408
--	---------

## CHAPTER XXIX.

Sulphur Dyestuffs: Constitution and Properties—Tendering Effect on Cotton—Assistants—Application to Cotton, Wool and Silk . . .	409-415
---	---------

## CHAPTER XXX.

Mordant Dyestuffs: Constitution and Application—Mordants and Assistants—Mordanting Wool, Cotton and Silk—Dyeing with Mordant Dyestuffs—Logwood—Logwood Black on Wool—Logwood on Cotton and Silk—Weighting of Silk in Logwood Dyeing—Fustic—Quercitron—Cutch—Cochineal—Kermes—Lac Dye—Madder—Alizarine on Wool and Cotton . . .	416-441
--	---------

## CHAPTER XXXI.

Aniline Black: Methods of Dyeing—Single-bath Aniline Black—Aged Aniline Black—Steamed Aniline Black . . .	442-447
---	---------

## CHAPTER XXXII.

Vat Dyestuffs: Indigoids—Indigotin—Indirubine—Synthesis of Indigo—Substituted Indigos—Thio-indigos—Anthraquinone Vat Dyestuffs—Indigosols—Application of Vat Dyestuffs to Cotton and Wool—Durindone Colours—Detection and Estimation of Indigo on Textile Fabrics . . .	448-459
---	---------

## CHAPTER XXXIII.

Mineral Pigments: Chrome Yellow—Iron Buff—Chrome Green—Mineral Khaki—Manganese Brown or Bistre—Prussian Blue . . .	460-462
--	---------

## CHAPTER XXXIV.

Scouring, Bleaching, and Dyeing of Rayons: Dyeing Regenerated Cellulose Rayons—Dyeing Acetyl Rayons—Saponification Method—Ionamines—Dispersed Dyestuffs—SRA Dyestuffs—Faults in Dyed Acetyl Rayon—Special Effects . . .	463-477
---	---------

## CHAPTER XXXV.

Pattern-Dyeing and Dyeing of Mixed Fibres: Cotton and Wool—Cotton and Silk—Silk and Wool—Mixtures containing Regenerated Cellulose—Mixtures containing Cellulose Acetate—Acetyl Rayon and Wool or Silk . . .	478-486
--	---------

## CHAPTER XXXVI.

Theory of Colour and Colour-Matching: The Spectroscope—Complementary Colours—Lovibond's Tintometer—Colour-Matching by Synthesis . . .	487-495
---	---------

## CHAPTER XXXVII.

Identification of Dyestuffs on Dyed Goods: Basic, Direct and Acid Dyestuffs—Sulphur, Mordant and Vat Dyestuffs—Single and Mixed Dyes . . .	496-498
--	---------

CHAPTER XXXVIII.

PAGES

The Examination of Dyestuffs: Identification of Class—Separation of Dyes of Same Class—Green's Method of Analysis—Analysis of Commercial Dyestuffs—Titration Processes—Dyeing Tests . . . . .	499-509
---	---------

CHAPTER XXXIX.

Damage and Defects: Defects in Undyed Materials—Defects due to Faults in Dyeing—Removal of Stains—Tenderness in Dyed Goods . . . . .	510-512
--	---------

CHAPTER XL.

The Preparation of Dyestuffs: General Principles—Acid Dyes—Basic Dyes—Direct Dyes—Sulphur Dyes—Mordant Dyes—Vat Dyes . . . . .	513-525
--	---------

ADDENDA.

Nylon—Vinyon—Recent Unshrinkable Finishes—High-temperature Method of Dyeing—Rate of Dyeing—Migration Properties—Dyeing Nylon . . . . .	526-530
--	---------

INDEX . . . . .	531-536
-----------------	---------



# THE BLEACHING, DYEING, AND CHEMICAL TECHNOLOGY OF TEXTILE FIBRES.

## CHAPTER I.

### THE HISTORY OF DYEING—PREPARATION OF DYESTUFFS—RELATION BETWEEN CHEMICAL CONSTITUTION AND COLOUR.

DYEING is the name given to the processes by which a comparatively permanent colour is imparted to certain bodies, of which the most important are the textile fibres. It appears that the production of cloth was soon followed by a demand for coloured fabrics, for the art of dyeing is of extreme antiquity. The earliest dyers were the Chinese and Indians, and it is difficult to decide which practised the art first. Dyed garments found in Egyptian tombs show that it was not very much later that the Egyptians learned how to dye, and it seems probable that the knowledge came to them from India through Asia Minor. The dyes used by the Ancients were extracted from plants or from insects; thus indigo was extracted from the indigo plant, and kermes, which is a red dye of great antiquity, and appears to be identical with cochineal, was obtained from an insect. It is astonishing, however, that the use of natural dyes should have been discovered so early, for comparatively complicated preliminary processes are always necessary when they are used. Thus kermes, like the majority of the natural dyes, will not permanently colour a textile fibre unless the latter has been subjected to a process known as mordanting. This consists in impregnating the fibre with a metallic hydroxide such as aluminium hydroxide  $[\text{Al}(\text{OH})_3]$ , tin hydroxide  $[\text{Sn}(\text{OH})_2]$ , chromium hydroxide  $[\text{Cr}(\text{OH})_3]$ , ferrous hydroxide  $[\text{Fe}(\text{OH})_2]$ , or ferric hydroxide  $[\text{Fe}(\text{OH})_3]$ . Indigo belongs to a class known as vat dyes, the members of which are all insoluble in water, and must therefore be converted into soluble compounds before they are of any use as dyestuffs. The vat dyes are made soluble by reducing them, and though the Ancients had not all our modern reducing agents at their disposal, yet they succeeded in bringing indigo into solution as indigo white by the aid of the reducing gases given off when organic matter is allowed to ferment, and of an alkali to dissolve the reduced indigo.

The writings of Pliny show that the Romans were well acquainted with the art of dyeing, and that alum was a mordanting agent commonly used at that time. Tyrian purple, the badge of royalty, is naturally associated with the Roman era of history, and this dye appears to have originated from the Phœnicians of Tyre. It was extracted from a shell-fish which inhabits the Mediterranean, and a modern investigation of its properties has shown that it is closely allied to indigo, and belongs to the vat dyes.

In the Middle Ages, Venice became the centre of dyeing, and from here the

knowledge of dyeing spread through Europe, though the use of a small number of dyes was already known. Thus Cæsar's writings show that woad was used in England so far back as 55 B.C. The discovery of America added logwood, fustic, and cochineal to the dyes at the disposal of Europe in the Middle Ages. Logwood soon became the most important dye for black shades, and it is interesting to note that this is one of the few dyes extracted from plants which is still extensively used. The development of trade with India brought indigo to Europe, but this dye met with great opposition in England at first, owing to the influence of the growers and users of woad, who feared that the introduction of this new and superior blue colour would ruin their trade.

No advances of great importance were made till 1856, when Perkin found that when aniline was oxidized under certain conditions it gave a mauve-coloured compound which might be used as a dye. This discovery opened a new era in the history of dyeing, as is obvious when one considers that, before 1856, the number of dyes known probably did not exceed one hundred, whilst to-day the number in use amounts to at least two thousand. The modern synthetic dyes are often known as the aniline dyes, but this name is misleading, for though Perkin's mauve and several other of the earlier dyes were made from aniline, the majority used now are not prepared from aniline. A better name is the coal-tar dyes, for almost without exception the starting-point in the preparation of modern dyes is a derivative of coal-tar.

The earliest synthetic dyes belonged to the group known as the basic dyes, of which magenta, malachite green, methyl violet, and Perkin's mauve are typical examples. These dyes will dye unmordanted wool and silk, but will not dye cotton till it has been impregnated with an acid mordant such as tannic acid. The basic dyes, however, suffer from the disadvantage of being comparatively insoluble in water, so that the discovery of Nicholson in 1862 that they could be converted into sulphonic acids, whose sodium salts were readily soluble in water, was one of great importance. The basic dye is converted to a sulphonic acid by a process known as sulphonation, which consists in heating it with strong sulphuric acid. This process replaces an atom of hydrogen in the molecule of the dye by the  $-SO_3H$  group, which gives acidic properties to the molecule, and converts the original basic dye into a sulphonic acid. A saturated solution of salt is usually added to the sulphonic acid, which converts the acid into its sodium salt, and at the same time causes it to be precipitated by a process of salting out. These sodium sulphonates belong to a class known as the acid dyes. They will dye unmordanted wool and silk, and cotton after it has been mordanted with a basic hydroxide, but as a class they are chiefly used for wool. Though practically all the acid dyes are sodium sulphonates, only a small number of them are prepared by sulphonating basic dyes, the majority of them being prepared by other methods.

Thus Perkin's discovery was soon followed by the preparation of numerous acid and basic dyes which were well adapted for dyeing silk and wool. These dyes, however, would not dye cotton till it had been subjected to the somewhat laborious process of mordanting, and it was not till some twenty-seven years later that any great advance was made in the dyeing of cotton. In the year 1884 Böttiger prepared Congo red, and he found that it would dye unmordanted cotton. This discovery opened a new field of investigation, the result of which is that we now have a large range of direct colours of almost every shade, all of which will dye cotton without the intervention of a mordant.

The basic, acid, and direct dyes are all classes which did not exist before 1857; but the older dyestuffs, namely, the mordant dyes and the vat dyes, have also received the attention of chemists in recent years, with the result

that many new members have been discovered, and many dyes which were formerly obtained only from natural sources are now prepared synthetically at less cost and in a purer state than before. Madder was one of the most important of the mordant dyes of the Middle Ages, and it was obtained from the root of the madder plant. This dye is now prepared exclusively from coal-tar products, and the cultivation of madder has been killed by the competition of the cheaper synthetic product. Indigo is perhaps the most important vat dye, and its cultivation has been one of the important trades of India. In 1897, however, synthetic indigo became a commercial product, and is now used extensively. Owing to their extreme fastness, the vat dyes are highly desirable for many purposes, but till recently only very few were known. Chemical investigations, however, have greatly increased the number of dyes of this very useful class, and a considerable range of colours is now obtainable.

Since coal-tar products play such an important part in the manufacture of dyes, it is necessary to include a brief description of these products in a study of dyeing. In the manufacture of coal-gas, the coal is heated in fireclay retorts, when coal-gas and coal-tar come over, leaving coke behind. The gases from the retort are passed through a series of upright tubes, in which the tar condenses, and from which it runs down into troughs, in which it is collected. The gas itself is not condensed by this process but passes on, and, eventually, after further purification, reaches the gasometer. The coal-tar obtained

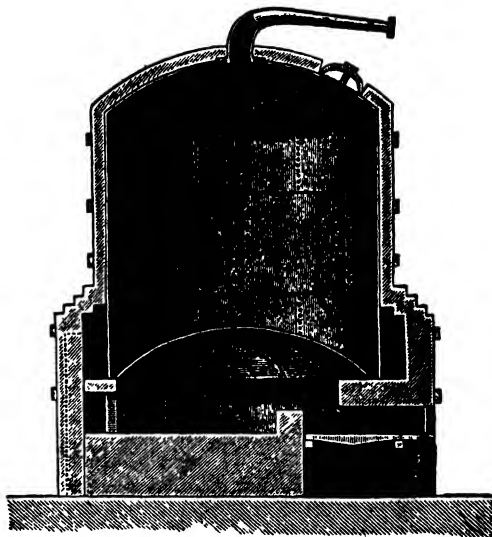


Fig. 1.—Coal-tar Still.

by the method described above is the most valuable by-product of the gas industry, for it consists of a mixture of products which are the starting-points in the manufacture of dyes and of many explosives. The crude coal-tar is put into a still such as the one shown in Fig. 1, and is usually distilled into four fractions.

The first fraction, consisting of *light oil*, is the portion which distils over below  $170^{\circ}$  C. This fraction consists chiefly of hydrocarbons, but some phenols and basic substances are present, which are removed by washing the oil with a solution of caustic soda and then with sulphuric acid. The oil remaining after this washing is redistilled, and three separate portions are collected. The first portion, which distils between  $82^{\circ}$  and  $110^{\circ}$  C., consists mainly of the hydrocarbon benzene, together with a little toluene; the second portion, collected between  $110^{\circ}$  and  $140^{\circ}$  C., consists of benzene, toluene, and xylene; whilst the last portion, which comes over between  $140^{\circ}$  and  $170^{\circ}$  C., consists mainly of the hydrocarbon xylene.

The second fraction obtained from the crude coal-tar is collected between  $170^{\circ}$  and  $230^{\circ}$  C., and is usually known as *middle oil*. This consists chiefly



of naphthalene and carbolic acid or phenol. When this fraction is cooled, the naphthalene crystallizes out, and the crystals are separated from the liquid carbolic acid and purified by washing with caustic soda and sulphuric acid. The liquor, after removal of the crystals, is shaken with caustic soda solution, when the phenol dissolves. The solution is separated from the impurities which do not dissolve, and decomposed with sulphuric acid. An oily layer of comparatively pure phenol separates out.

The third fraction, collected between 230° and 270° C., is known as *heavy oil* or *creosote oil*. This consists of carbolic acid, cresols—which are compounds similar to carbolic acid—and naphthalene. This fraction is not as a rule separated into its constituents, but is used as it is as a timber preservative.

The last fraction is that which comes over above 270° C., and is known as *anthracene oil*. This consists mainly of the hydrocarbon anthracene, which crystallizes out as the distillate cools. Finally, there remains in the still a portion which will not distil, and which is the pitch extensively used in making roads.

Practically every dyestuff is made from one or other of the compounds obtained by the distillation of coal-tar. The chief of these are

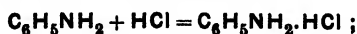
Benzene . . .	$C_6H_6$	Toluene . . .	$C_6H_5.CH_3$ or $C_7H_8$
Naphthalene . . .	$C_{10}H_8$	Anthracene . . .	$C_{14}H_{10}$
Phenol . . .	$C_6H_5.OH$	Cresol . . .	$C_7H_7.OH$
Acridine . . .	$C_{13}H_9N$	Quinoline . . .	$C_9H_7N$

These compounds are, however, a long way removed from the dyestuffs, and they must first be changed into others termed *intermediates*. These are hydrocarbons in which one or more of the hydrogen atoms are replaced by such groups as the nitro group ( $-NO_2$ ), amino group ( $-NH_2$ ), hydroxyl group ( $-OH$ ), sulphonic-acid group ( $-SO_3H$ ), and others. Examples of such intermediates are

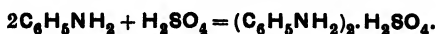
Nitrobenzene . . . . .	$C_6H_5.NO_2$
Aniline . . . . .	$C_6H_5.NH_2$
$\alpha$ - or $\beta$ -Naphthol . . . . .	$C_{10}H_7.OH$
$\alpha$ - or $\beta$ -Naphthalene-sulphonic acid . . . . .	$C_{10}H_7.SO_3H$

The two most important classes of dye intermediates are the amines and the sulphonic acids, and these classes may be described briefly.

**The Amines.**—The amines are organic bases, since they combine with acids to form salts. They invariably contain an amino group ( $-NH_2$ ) or a modified amino group. Primary amines have the general formula  $RNH_2$ , secondary amines have the formula  $R^1NHR^2$ , and tertiary amines  $R^1NR^2R^3$ . Aniline,  $C_6H_5NH_2$ , is a primary amine; methylaniline,  $C_6H_5NH(CH_3)$ , is a secondary amine, and as an example of a tertiary amine, dimethylaniline,  $C_6H_5N(CH_3)_2$ , may be given. All three types of amines, though basic, do not form salts in exactly the same way as do the inorganic bases, for no water is eliminated during the reaction. The organic base merely unites with a molecule of the acid as shown in the equations:



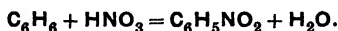
Aniline                      Aniline hydrochloride



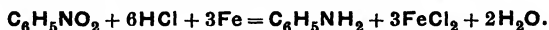
Aniline                      Aniline sulphate

The amines are not soluble in water, but their salts are as a rule soluble. Organic bases may, therefore, be dissolved in acids. A notable exception to this rule is the fact that aniline sulphate is sparingly soluble in water.

Organic bases are prepared from coal-tar derivatives in various ways. Aromatic hydrocarbons react with nitric acid to give nitro compounds. Thus benzene and nitric acid give nitrobenzene:



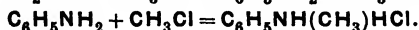
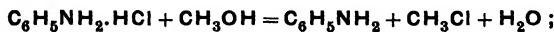
These nitro compounds may be reduced to primary amines. Nitrobenzene when reduced with iron and hydrochloric acid gives aniline:



This is the principle of the commercial processes by which aniline is obtained. Benzene is nitrated in nitrating pans which have a capacity of 1600 gallons. The pan is provided with stirrers and internal cooling pipes through which cold water runs, in order that the reacting mixture may not become too hot. When 500 gallons of benzene have been run into the pan the stirrer is set in motion, and a mixture of sulphuric and nitric acids (containing 60 parts by weight of nitric acid and 90 parts of sulphuric acid) is slowly added. The mixture is vigorously stirred, and the temperature is at first kept between  $40^\circ$  and  $50^\circ$  C., but towards the end it is allowed to rise to  $60^\circ$  C. Sulphuric acid is added to the nitric acid because it is found that its presence enables the nitration to be carried out both at a lower temperature and with greater rapidity. When nitration is complete, the mixture is run into washing-tanks and freed from excess of acid by washing with water and alkali.

Nitrobenzene is commercially reduced to aniline with iron and hydrochloric acid. The iron turnings are put into the vessel in which the reduction is to be carried out, and the nitrobenzene and hydrochloric acid are slowly run in. Steam is blown in to warm the mixture and so hasten the reduction, and a condenser is fitted to the vessel in such a manner that no steam or nitrobenzene can escape. During the operation the mixture is agitated with a mechanical stirrer. At the end of the reduction the aniline is run off, washed with water, and finally purified by distillation under reduced pressure. Many other amines are prepared in the same way, and toluidine, for instance, can be made by nitrating toluene and subsequently reducing the nitrotoluene.

Methylaniline is prepared by heating a mixture of aniline with hydrochloric acid and methyl alcohol to  $200^\circ$  C. in a closed vessel. Aniline hydrochloride is first formed, which reacts with methyl alcohol giving methyl chloride, and the latter, in turn, reacts with aniline giving the hydrochloride of methylaniline. The course of the reaction is therefore represented by the following equations:

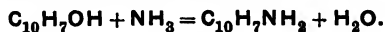


If a larger proportion of methyl alcohol be used, dimethylaniline,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ , is obtained.

The naphthylamines are derivatives of naphthalene, and are of great importance in the dye industry. The two forms,  $\alpha$ - and  $\beta$ -naphthylamine, have the following structural formulæ:

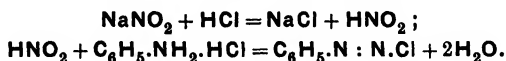


$\beta$ -Naphthylamine is commercially prepared by heating ammonia and  $\beta$ -naphthol under pressure, when the following reaction takes place:



$\alpha$ -Naphthylamine may be prepared either by reducing the corresponding nitronaphthalene or by heating  $\alpha$ -naphthol with ammonia and zinc chloride.

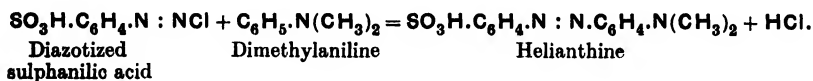
Primary aromatic amines undergo a very important change when treated with nitrous acid. This change is known as *diazotization*, and the new product is called a diazonium compound. Diazotization is usually carried out by dissolving the base in hydrochloric acid, care being taken that excess of acid is used, for sodium nitrite is next added, and it is important that there should be enough acid to liberate the nitrous acid from the nitrite. The reaction then goes in two stages: first sodium nitrite and hydrochloric acid give nitrous acid, and then nitrous acid and aniline hydrochloride give the diazonium salt:



These diazonium compounds are very unstable, and are very rarely prepared in the solid state, always being used in solution. They undergo many important reactions, but the so-called *coupling* is the only one which concerns the dyer. When a solution of a diazonium salt is added to an alkaline solution of a phenol the two combine, giving a coloured product known as an *azo compound*. Thus phenol and benzenediazonium chloride react in the following way:



Diazonium compounds couple with bases in a similar way: thus diazotized sulphanilic acid and dimethylaniline couple to give the dyestuff known as helianthine:

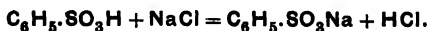


This reaction plays an important part both in the manufacture of dyestuffs and in the application of dyes to the textile fibres.

**The Sulphonic Acids.**—These form another class of dyestuff intermediates of extreme importance. Sulphonic acids are prepared by the process known as *sulphonation*, which consists, as a rule, in heating the organic compound with strong or fuming sulphuric acid. When benzene is heated with about twice its weight of sulphuric acid for some time, with constant or occasional stirring, it is slowly dissolved, and benzenesulphonic acid is formed in the following way:



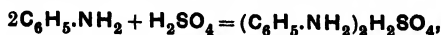
The sulphonic acids have the properties of relatively strong acids. They are soluble in water, and are as a rule hygroscopic substances. They are usually handled in commerce in the form of their sodium salts, for the latter are precipitated when a strong solution of salt is added to a crude sulphonation product:



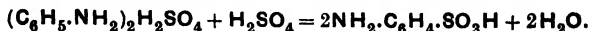
Naphthalene is sulphonated in the same way as benzene, and its sulphonic acids are of great importance in the dye industry.

Amines and phenols, as well as aromatic nitro compounds, may also be

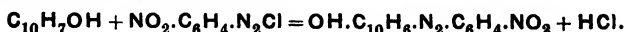
sulphonated. When aniline is heated with sulphuric acid it is converted into sulphanilic acid. Aniline sulphate is first formed :



and the sulphate is then changed to sulphanilic acid under the influence of heat :



Intermediates are, as a rule, colourless compounds. By means of suitable chemical reactions other groups are introduced which give rise to bodies of more complex structure, which in many cases are dyestuffs. For example,  $\beta$ -naphthol is a colourless compound with a comparatively simple structure. When it is treated with a solution of diazotized *para*-nitraniline, the two bodies combine with the elimination of hydrochloric acid, and a much more complex molecule is produced, which is a dye :



Two other examples of the way in which intermediates are changed into dyestuffs are given :

(1) Para-rosaniline is one of the earliest known coal-tar dyes. It is prepared by oxidizing a mixture of aniline and para-toluidine,  $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , with arsenic pentoxide,  $\text{As}_2\text{O}_5$  :

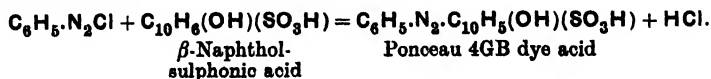


The oxygen is given up by the arsenic pentoxide in accordance with the equation :



The product of this reaction is a compound called the *colour base* of para-rosaniline. It is a colourless compound, but it possesses basic properties, and forms highly coloured salts with acids, and these are the dyestuffs. The actual salt used in commerce is the hydrochloride, which is obtained by adding hydrochloric acid to the colour base. More modern processes have now displaced the one described above for the manufacture of this dye. Amongst these is the formaldehyde process, in which use is made of a compound known as anhydro-formaldehyde aniline, which is obtained when formaldehyde reacts with aniline. Aniline and formaldehyde are mixed together, and an oily mass separates out, which soon solidifies. The solid is separated from the liquid layer, and a white powdery mass of anhydro-formaldehyde aniline is obtained. This product is mixed with aniline, aniline hydrochloride, nitrobenzene, and ferric chloride, and heated to  $170^\circ\text{C}$ . When it has been heated sufficiently any unchanged aniline and nitrobenzene are distilled off with steam, and the pararosaniline which is formed is extracted from the remaining solid with dilute acetic acid. When a strong solution of salt is added to this solution of para-rosaniline the dye is thrown out of solution, and may be collected by filtration.

(2) The preparation of the acid dyestuff Ponceau 4GB may also be quoted as an example. Aniline is dissolved in hydrochloric acid and diazotized. The solution of the diazonium salt is added to an aqueous solution of  $\beta$ -naphthol-sulphonic acid. Coupling takes place, and the acid of the dye Ponceau 4GB is formed according to the following equation :



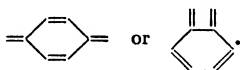
The dyestuff itself is the sodium salt of this acid, and is obtained by "salting out" with a saturated salt solution.

These examples show that the preparation of dyestuffs from coal-tar is by no means a simple process. The various constituents of the tar must first be separated by distillation and purified. These are next converted into intermediates by such processes as nitration and sulphonation, and finally the intermediates are converted into dyestuffs by still more complicated chemical reactions.

**Colour.**—At first sight it does not seem very astonishing that a deeply coloured solution of a dyestuff should permanently colour a textile fabric. Closer examination shows that the phenomenon is really rather remarkable, for it is by no means every coloured solution which has this property. Many coloured solutions will stain textile fabrics but will not dye them; that is to say, the stain is readily removed by washing with water. In order that the fibre may be dyed, the colour must be retained by it either in chemical combination or in a physical condition different from the normal.

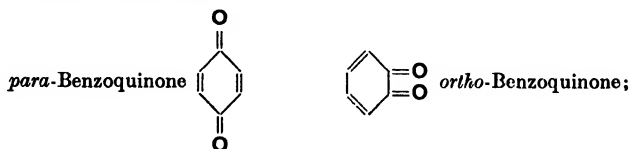
In order that this may occur, it is found, in the first place, that the molecule of the dyestuff must be comparatively complex. But molecular complexity alone is not sufficient, for very many organic compounds of high molecular complexity are not even coloured.

Many colourless organic compounds become coloured on the introduction of certain groups known as *chromophores*. Of these the most important are the azo group ( $-N=N-$ ), the nitro group ( $-NO_2$ ), the nitroso group ( $-NO$ ), the carbonyl group ( $-CO-$ ), and the quinonoid group,

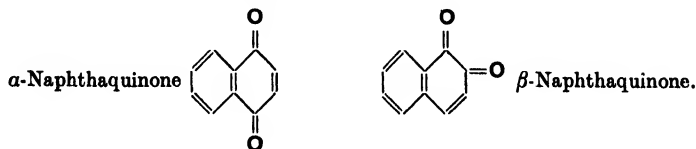


Whenever a compound contains one of the above groups in its molecule it is coloured. The first four groups mentioned have for a long time been recognized as chromophores, but it was known that a large number of compounds were highly coloured in spite of the fact that they contained none of the known chromophores. There must therefore be some unknown chromophore, and this was subsequently supplied by the *para*- and the *ortho*-quinonoid groupings. The simple quinones are all coloured, and exist in two forms in the cases of both benzene and naphthalene.

The two benzoquinones are



and the two naphthaquinones are



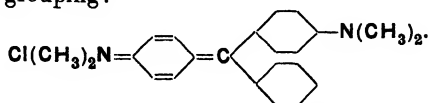
A great many dyestuffs can be represented as being built up on the type of either *ortho*- or *para*-quinone, in which the O-atoms are replaced by complex groups. Methylene blue is a dyestuff containing the *ortho*-quinonoid group as

## CHEMICAL CONSTITUTION AND COLOUR.

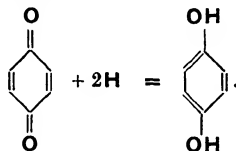
its chromophore, its structural formula being as shown :



and Malachite Green may be given as an example of a dyestuff containing the *para*-quinonoid grouping:

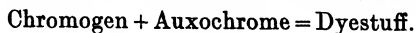


The quinonoid theory of colour is of interest also, because it explains how some of the dyestuffs can be reduced to colourless (or leuco) compounds which regenerate the colouring matter on oxidation. Quinone itself is a coloured compound. When it is treated with nascent hydrogen it is reduced to hydroquinone, which is colourless:



This reaction is accompanied by a change from the quinonoid to what is termed the benzenoid form. When hydroquinone is treated with a suitable oxidizing agent, such as ferric chloride, the two atoms of hydrogen of the hydroxyl groups are removed as water, and the original quinone is reproduced. This reaction is general to any dyestuff which contains either the *ortho*- or the *para*-quinone grouping. Those containing the *ortho*-quinone group, however, give leuco compounds which, as a rule, are oxidized more easily than those which contain the *para*-quinone group.

A molecule which contains a chromophore is called a *chromogen*. But a chromogen is not a dyestuff, although it is predisposed to become one under suitable conditions. In order to transform the chromogen into a dyestuff another grouping termed an *auxochrome* must be introduced. Among important auxochromes are the hydroxyl ( $-\text{OH}$ ) and amino ( $-\text{NH}_2$ ) groups, and substituted amino groups such as  $-\text{N}(\text{CH}_3)_2$  and  $-\text{NH}(\text{C}_2\text{H}_5)$ . Thus the formation of a dyestuff may be represented by the equation:



Azobenzene,  $\text{C}_6\text{H}_5\text{N}:\text{N}.\text{C}_6\text{H}_5$ , is a chromogen, since it contains the azo group,  $-\text{N}=\text{N}-$ , as a chromophore. It has a brilliant red colour, but is not a dyestuff. It would stain a fabric, but the colour would be removed completely by washing with water. When an amino group is introduced the product is a dyestuff,  $\text{C}_6\text{H}_5\text{N}_2.\text{C}_6\text{H}_4.\text{NH}_2$ . In the case of Ponceau, described above, we made two bodies, diazobenzene chloride and  $\beta$ -naphthol-sulphonic acid. The former contains the chromophore group  $-\text{N}=\text{N}-$ , while the latter contains the auxochrome group  $-\text{OH}$ . Neither body was itself a dyestuff or even coloured; but when they were allowed to combine the new compound produced contained both chromophore and auxochrome groups, and was the dye acid of Ponceau.

## CHAPTER II.

### COMMERCIAL DYESTUFFS—GENERAL CONDITIONS OF DYEING.

COMMERCIAL dyestuffs are not, as a rule, pure substances. Many of them are salted out from their solutions, and hence contain sodium chloride or sodium sulphate. The percentage of dyestuff can be determined in most cases by chemical analysis or approximately by quantitative dyeing trials.

Dyestuffs do not always consist of one chemical compound. They may be mixtures, made for the purpose of producing a colour which cannot be obtained with a single dyestuff, or for improving the shade of a particular dyestuff. The following simple tests may be applied to determine whether a dyestuff is a mixture:

(1) A little of the finely powdered sample is placed on a slip of dry paper and blown horizontally across the surface of a piece of blotting-paper moistened with water. In the case of a mixture, differently coloured spots may be produced.

(2) A similar result is obtained by sprinkling the powdered dyestuff over the surface of concentrated sulphuric acid.

(3) The capillary test is often useful. Some of the dyestuff is dissolved in water and placed in a flat-bottomed dish. A strip of blotting- or filter-paper about 1 inch wide and 12 inches long is suspended vertically with its lower end dipping beneath the surface of the solution. If the dyestuff is a mixture the different constituents will generally rise to different heights on the paper, giving a zone of uniform colour changing gradually into bands of different colours.

**Nomenclature of Dyestuffs.**—There are two ways of naming a chemical compound. The first is to give it a name which describes its chemical composition, the second to give it a fancy name which conveys no definite information. The term "ferrous sulphate," for example, suggests the chemical constitution of the compound, but "copperas" tells nothing. Dyestuffs are almost always known by fancy names, such as "ponceau," "fuchsine," "chrysophenine," etc. The same dyestuff may have also different names; for example, "iso-purpurine" and "Alizarine GP" are identical in composition and dyeing properties. Capital letters are commonly put after the name of a dyestuff. These may be a private mark of the manufacturer, or used to indicate some peculiarity or property of the dyestuff. Thus "B" indicates a blue, "R" a red, and "Y" a yellow shade. The strength of shade is usually indicated by repetition of the capital letter. Thus "B" means a blue shade, "BB" a bluer, and "BBB" a still bluer shade. Sometimes numerals are used instead of repeating the capital letter, *e.g.* "3B." Another method is the use of the letter "X." Thus, "Alizarine GX" would mean a strong green shade. The letter "S" indicates solubility in water, *e.g.* "Naphthol Yellow S."

**Classification of Dyestuffs.**—Dyestuffs are classified primarily according to

their dyeing properties, although the members of each class have the same general chemical affinities. These classes are as follows:

(1) *Acid Dyestuffs*.—These are sodium salts, usually of sulphonic acids, but in a few cases of carboxylic acids. They dye both wool and silk, and are used for both. They have no affinity for vegetable fibres.

(2) *Basic Dyestuffs*.—These are hydrochlorides of organic bases. They dye animal fibres directly, giving very bright colours, but have little affinity for vegetable fibres. They are used chiefly for wool and silk.

(3) *Direct or Substantive Dyestuffs*.—Like acid dyestuffs these are also sodium salts of sulphonic acids, but are characterized by their ability to dye both animal and vegetable fibres. They are used for cotton, wool, silk, and rayon, and for goods containing two or more different fibres.

(4) *Sulphur Dyestuffs*.—These contain sulphur but are not salts of sulphonic acids. They are insoluble in water, but dissolve in an alkaline solution of sodium sulphide. They dye all fibres directly, but owing to the alkalinity of the dye-bath are used principally for cotton.

(5) *Mordant Dyestuffs*.—This group includes many natural dyestuffs, such as logwood, alizarine, cochineal, etc., and a large number of artificial dyestuffs derived chiefly from anthracene. The members of this group are generally insoluble in water. They have no natural affinity for textile fibres, but combine with certain metallic oxides to form insoluble coloured compounds. Dyeing consists of two processes: (a) mordanting the goods with a metallic oxide; and (b) dyeing proper. Mordant dyestuffs are *polygenetic*—that is, they give different colours depending upon the metallic oxide used as the mordant. They are used largely for woollen goods when a fast colour is required.

(6) *Vat Dyestuffs*.—Indigo is a vat dyestuff and is typical of the class. It is insoluble in water, but when reduced it gives a leuco compound which dissolves in sodium hydroxide solution. The material to be dyed is impregnated with the alkaline solution of the leuco compound, and then oxidized to reproduce the insoluble dyestuff. All fibres can be dyed, but the alkalinity of the bath is in some cases too great for wool.

(7) *Dyestuffs built up on the Fibre*.—Some of the most useful colours cannot be used in the form of dyestuffs owing to their insolubility, and are made on the fibre from simpler intermediates. Aniline black is produced by the oxidation of aniline, and other colours are obtained from different bases. The azoic colours, which are used extensively for cotton, are applied by treating the fibre with a phenolic compound, such as  $\beta$ -naphthol or naphthol AS, and then coupling with a diazotized base.

(8) *Mineral Pigments*.—These are obtained by precipitating a coloured metallic compound on the fibre by a double decomposition. Thus, Prussian blue is formed by treating the goods with a solution of a ferric salt followed by one containing potassium ferrocyanide. Khaki consists of a mixture of suitable proportions of ferric and chromium oxides, and may be produced by impregnating goods with a solution of ferric and chromic chlorides and then immersing them in a bath containing sodium hydroxide.

**General Conditions of Dyeing.**—Before goods can be dyed they must be freed from all impurities which would prevent penetration of the dye liquor or affect the colour of the dyestuff. This condition is ensured by a suitable process of scouring, sometimes followed by bleaching. The dyestuff is applied in a bath containing water and generally one or more chemicals known as *assistants*. After dyeing, the goods are washed thoroughly with water, and may also be “after-treated” to improve the colour or its fastness. The object of the dyer is to produce a uniform colour of the required shade. Many factors



affect the result. These will be discussed later, but there are two which overshadow all the others in importance. These are (*a*) perfect permeability of the goods and their freedom from impurities which would prevent the even distribution of the dyestuff; and (*b*) the quality of the water used. It is essential that the dyer should have knowledge of the chemical and physical properties of the various fibres, and of the chemistry of the substances and processes employed in their treatment.

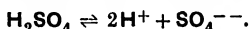
## CHAPTER III.

### IONIZATION—HYDROGEN-ION CONCENTRATION—THE MICROSCOPE—COLOUR MEASUREMENT.

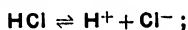
BEFORE proceeding to the study of textile fibres and dyestuffs, it will be useful to describe a few of the special phenomena and methods of technique, an understanding of which is essential to those who wish to become proficient in textile technology.

#### Ionization.

*Ionization* is the name given to a particular type of reversible reaction, exhibited by all acids, alkalis, and salts when dissolved in water. Bodies are regarded as composed of *ions*, which carry either positive or negative electrical charges. In sulphuric acid, for example, the ions are  $2\text{H}$  and  $\text{SO}_4$ . Each  $\text{H}$ -ion bears a positive charge and the  $\text{SO}_4$ -ion two negative charges. These are written  $2\text{H}^+$  and  $\text{SO}_4^{--}$ , and the splitting up into ions, when the compound is dissolved in water, is represented by the equation:



Similarly with other common acids:



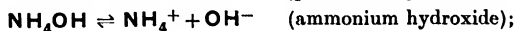
and



Alkalis also are ionized when dissolved in water, but they give metallic and hydroxyl ions. Thus, sodium hydroxide gives positively charged sodium ions and negatively charged hydroxyl ions:



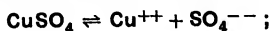
Similarly:



and



So far, only acids and bases have been considered, but salts also undergo ionization. Copper sulphate ionizes to copper ions and  $\text{SO}_4$ -ions:



similarly,



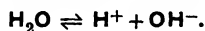
The general name of *electrolyte* is given to all bodies which ionize in solution. Since ionization is a reversible reaction, a state of equilibrium will always be attained in a solution of an electrolyte.

### Hydrogen-ion Concentration (pH-value).

There are few processes in the dyeing, scouring, or bleaching of textiles in which acidity and alkalinity are not important factors. In ordinary conversation acids or alkalis are described as "strong" or "weak," but such terms are far too indefinite for accurate descriptions of process requirements. An instruction to make a liquor faintly acid can mean anything according to the interpretation placed on the word "faintly."

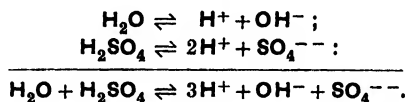
Fortunately we have at our disposal a universally applicable method of expressing acidity or alkalinity with accuracy, which depends on the concentration of the hydrogen ions in the liquid.

Pure water dissociates to a very small extent into positively charged hydrogen ions and negatively charged hydroxyl ions:



In the case of water the number of hydrogen ions is exactly equivalent to the number of hydroxyl ions, and water is therefore neutral in reaction.

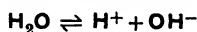
When acids are dissolved in water they dissociate with the formation of further hydrogen ions but without producing a corresponding number of hydroxyl ions. The relative concentration of hydrogen ions is therefore greatly increased:



Those properties common to all acids, generally termed *acidity*, are due solely to the activity of the hydrogen ions.

It is therefore obvious that any means of expressing the concentration of the hydrogen ions will give us a measure of the "acidity."

At first sight, however, it is not quite so obvious that the number of hydrogen ions in a solution can also express its alkalinity. But the equation:



is reversible, and this means that increasing the hydroxyl-ion concentration, which is brought about by alkalis, progressively decreases the hydrogen-ion concentration, but never brings it down to zero. Thus even in alkaline solutions hydrogen ions are present, and their concentration may therefore be used to measure alkalinity.

In pure water the hydrogen-ion concentration amounts to 1 in 10,000,000, i.e. the concentration is  $10^{-7}$ . The logarithm of this is  $-7$ , and if we omit the minus sign we arrive at the figure of 7, which is the pH ( $p$  representing "pressure," which is equivalent to "concentration," of hydrogen ions) of neutral water.

When equivalent weights of acids and alkalis are dissolved in water they do not necessarily dissociate to the same extent. Thus 1 millilitre of decinormal sulphuric acid neutralizes the same weight of sodium hydroxide as 1 ml. of decinormal acetic acid; but the hydrogen-ion concentration of the sulphuric acid is much greater than that of the acetic acid. That is, the hydrogen-ion concentration is not a measure of the neutralizing power of an acid, but only of its degree of acidity. In common words we say that sulphuric acid is "stronger" than acetic acid, meaning that when equivalent weights of the two acids are dissolved in water, the "stronger" has a greater hydrogen-

ion concentration than the "weaker." Equally, decinormal solutions of sodium hydroxide and sodium carbonate will neutralize the same weight of sulphuric acid, but, again, have different hydrogen- (or hydroxyl-) ion concentrations. Hence we say that the degree of alkalinity of sodium hydroxide is greater than that of sodium carbonate, or that it is a stronger alkali.

The negative logarithm of the hydrogen-ion concentration of acids or alkalis is termed the *pH*-value.

**Sørensen's Method of expressing *pH*-values.**—If a solution has a hydrogen-ion concentration ten times greater than that of water, this would be  $10 \times 10^{-7}$ . If this multiplication is performed by logarithms, the logarithm of the product is

$$\log 10 + \log 10^{-7} = 1 - 7 = -6.$$

Sørensen uses the figure 6, omitting the minus sign, to express the degree of acidity (*pH*). Table I gives the hydrogen-ion concentrations corresponding to *pH*-values of from 1 to 13.

TABLE I.—HYDROGEN-ION CONCENTRATIONS AND *pH*-VALUES.

H-ion Concentration.	<i>pH</i> -value.	Reaction.
$1,000,000 \times 10^{-7}$	1	Acid solutions
$100,000 \times 10^{-7}$	2	
$10,000 \times 10^{-7}$	3	
$1,000 \times 10^{-7}$	4	
$100 \times 10^{-7}$	5	
$10 \times 10^{-7}$	6	
$1 \times 10^{-7}$	7	Neutral
$0.1 \times 10^{-7}$	8	Alkaline solutions
$0.01 \times 10^{-7}$	9	
$0.001 \times 10^{-7}$	10	
$0.0001 \times 10^{-7}$	11	
$0.00001 \times 10^{-7}$	12	
$0.000001 \times 10^{-7}$	13	

**Buffered Solutions.**—For many purposes it is desirable to prepare solutions of known *pH*-values. This is particularly important when standards of comparison are needed in the determination of *pH* by the methods described later. The very smallest traces of the stronger acids or alkalis make a very great difference to the *pH*-value of a solution. This is not the case with weak acids or alkalis. In preparing standard-*pH* solutions it is therefore common to add salts or weak acids or bases to prevent small traces of stronger acids or alkalis from unduly influencing the hydrogen-ion concentration. The effect of this addition is that traces of stronger acids or alkalis will liberate the weakly dissociated component. Such salts are called *buffers*, and the solutions to which they are added are called *buffered liquors*.

The effect is well illustrated by the titration curves *A* and *B* (Fig. 2). In curve *A* the *pH* is plotted against the addition of 0.1*N.* sulphuric acid to a solution containing 5 ml. of 0.1*N.* sodium hydroxide. In curve *B* the same titration is shown, with the difference that 5 g. of sodium acetate, which is the "buffer," has been added. In curve *A* the gradient is so steep that the addition of 1 ml.

of acid makes a difference of 4.5 units in the  $pH$ . In curve *B*, however, each ml. of acid alters the  $pH$  by only 0.5 unit. This is a very clear demonstration of how a buffer damps down the alteration in hydrogen-ion concentration brought about by traces of strong acids.

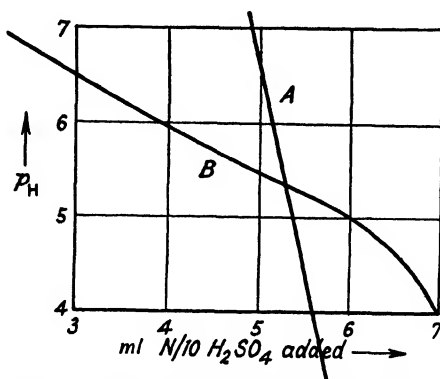


Fig. 2.—Effect of Buffer Solution of Sodium Acetate on  $pH$ -value.

Salts commonly used for buffering are—

Potassium hydrogen phthalate,  
Potassium dihydrogen phosphate,

Potassium borate,  
Sodium acetate.

Table II gives a method of preparing a range of solutions of standard  $pH$ -values. The standard solutions required are—

Solution 1: 0.2M. Potassium hydrogen phthalate (40.843 g. per litre).

Solution 2: 0.2M. Potassium dihydrogen phosphate (27.218 g. per litre).

Solution 3: 0.2M. Boric acid (12.369 g. per litre) and

0.2M. Potassium chloride (14.911 g. per litre).

Solution 4: 0.2M. Sodium hydroxide (carbonate-free), in a paraffined bottle.

Solution 5: 0.2M. Hydrochloric acid.

The mixtures shown in Table II of the above solutions, when diluted to 200 ml., give the  $pH$ -values indicated.

**Determination of  $pH$ -value by Colorimetric Methods.**—Chemicals termed *indicators* possess the common property of changing colour over a definite range of  $pH$ -values. Litmus, for instance, is red at a  $pH$  of 5 or less and blue at a  $pH$  of 8 or more; within the  $pH$ -range of 5 to 8 it changes from red through purple to blue. The changes of various indicators are given in Table III.

It will be apparent that with such a range of indicators available it is quite possible to determine  $pH$ -values by trying indicators in turn and seeing which one changes colour in the solution. Where accuracy is required, the actual colour produced with the indicator is compared with those of buffered solutions, prepared as described in the last paragraph, to which the same indicator has been added.

**Mixed Indicators.**—By mixing indicators it is possible to obtain a continuous gradation of colour over a wide range of  $pH$ -values. One

TABLE II.—PREPARATION OF STANDARD BUFFERS.

<i>pH</i> .	First Component, ml.	Second Component, ml.	<i>pH</i> .	First Component, ml.	Second Component, ml.
	Solution 1.	Solution 5.		Solution 2.	Solution 4.
2.2	50	46.7	6.4	50	12.6
2.4	50	39.6	6.6	50	17.8
2.6	50	32.95	6.8	50	23.65
2.8	50	26.42	7.0	50	29.63
3.0	50	20.32	7.2	50	35.0
3.2	50	14.7	7.4	50	39.5
3.4	50	9.9	7.6	50	42.8
3.6	50	5.97	7.8	50	45.2
3.8	50	2.63	8.0	50	46.8
	Solution 1.	Solution 4.		Solution 3.	Solution 4.
4.0	50	0.4	8.2	50	5.9
4.2	50	3.7	8.4	50	8.5
4.4	50	7.5	8.6	50	12.0
4.6	50	12.15	8.8	50	16.3
4.8	50	17.7	9.0	50	21.3
5.0	50	23.85	9.2	50	26.7
5.2	50	29.95	9.4	50	32.0
5.4	50	35.45	9.6	50	36.85
5.6	50	39.85	9.8	50	40.8
5.8	50	43.0	10.0	50	43.9
6.0	50	45.45			
6.2	50	47.0			

TABLE III.—COLOUR CHANGES AND *pH*-RANGES OF INDICATORS.

Indicator.	<i>pH</i> .	Colour.	<i>pH</i> .	Colour.
Cresol red . . . . .	0.2	red	1.8	yellow
<i>meta</i> -Cresol purple . . . . .	1.2	red	2.8	yellow
Thymol blue . . . . .	1.2	red	2.8	yellow
Methyl orange . . . . .	2	red	4	orange-yellow
Bromophenol blue . . . . .	2.8	yellow	4.6	violet
Congo red . . . . .	3	blue	5	red
Bromocresol green . . . . .	3.6	yellow	5.2	blue
Methyl red . . . . .	4.4	red	6	yellow
Chlorophenol red . . . . .	4.6	yellow	7	red-violet
Litmus . . . . .	5	red	8	blue
Bromocresol purple . . . . .	5.2	yellow	6.8	purple
Bromothymol blue . . . . .	6	yellow	7.6	blue
Phenol red . . . . .	6.8	yellow	8.4	red
Cresol red . . . . .	7.2	yellow	8.8	red-violet
Brilliant yellow . . . . .	7.2	yellow	8.4	yellow-red
<i>meta</i> -Cresol purple . . . . .	7.4	yellow	9	red-violet
Turmeric . . . . .	7.8	yellow	9.2	brown
Thymol blue . . . . .	8	yellow	9.6	blue-violet
Phenolphthalein . . . . .	8.5	colourless	10.5	red

well-known example is the B.D.H. Universal Indicator, which is active over the following range:

pH.	Colour.	pH.	Colour.
Up to 3 . . .	Red	8 . . .	Green
4 . . .	Deeper red	8.5 . . .	Bluish-green
5 . . .	Orange-red	9 . . .	Greenish-blue
5.5 . . .	Orange	9.5 . . .	Blue
6 . . .	Orange-yellow	10 . . .	Violet
6.5 . . .	Yellow	10.5 . . .	Reddish-violet
7.0 to 7.5 . . .	Greenish-yellow	11 . . .	Deeper reddish-violet

Colorimetric determinations of  $pH$ -values are best carried out in *comparators*. The simplest form (Fig. 3) consists of a block of wood with six vertical holes

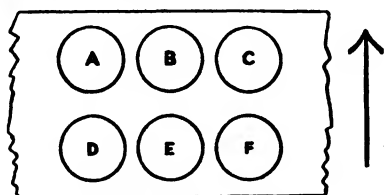


Fig. 3.—Comparator.

capable of taking boiling-tubes or test-tubes, each pair of these holes being traversed by horizontal slits, through which the colours can be seen and compared.

The sample and the indicator are placed in the centre aperture, and standard buffered solutions containing the same indicator are tried with different  $pH$ -values in holes *D* and *F* (Fig. 3) until one is found giving exactly the same colour. Tubes containing the sample only are placed behind the

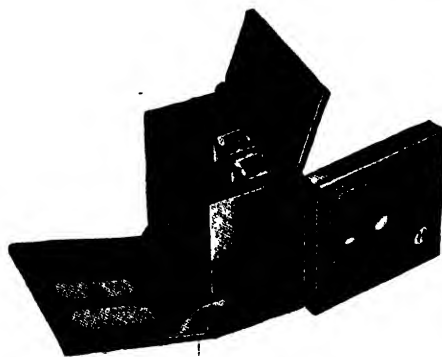


Fig. 4.—Lovibond Comparator.

buffered solutions to compensate for any distortion of the coloration of the indicator caused by the colour of the sample itself.

Very simple comparators are now constructed using discs containing transparent coloured insertions which correspond with the tint of the indicator chosen (Fig. 4). This dispenses with the necessity of making up buffered solutions, and the discs are permanent and do not suffer from fading.

**Electrometric Determination of  $pH$ -values.**—When any metal is immersed in a solution containing ions of the same metal, an E.M.F. is set up between the metal and the solution, its value depending on the concentration of the

metallic ions. In the same way, when a hydrogen electrode (obtained by the absorption of hydrogen on platinum black) is immersed in a solution, an E.M.F. will be produced, the actual voltage being determined by the concentration of the hydrogen ions. This is the principle underlying the electrometric estimation of *pH*.

*Hydrogen Electrode.*—A simple form of hydrogen electrode is illustrated in Fig. 5. It consists essentially of a piece of platinum foil about  $\frac{1}{4}$  sq. inch in area, connected through a tube to the volt-measuring apparatus. The outer

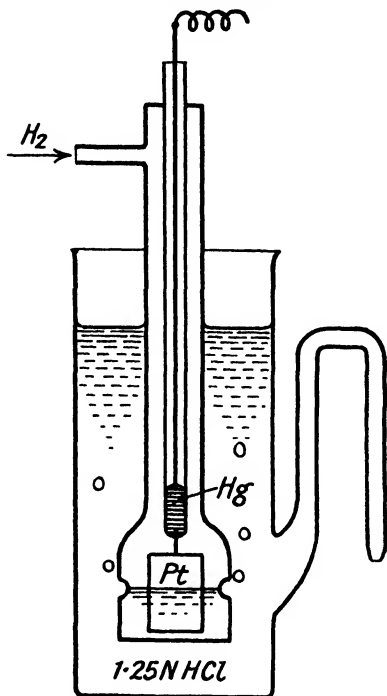


Fig. 5.—Hydrogen Electrode.

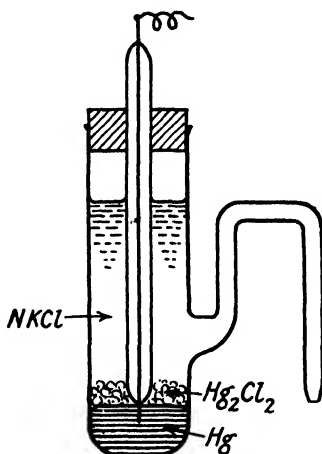


Fig. 6.—Normal Calomel Electrode.

case is so constructed that hydrogen can continually be passed over the platinum, at the same time permitting the latter to be immersed in the liquid under examination.

*Calomel Electrode.*—It is not possible to measure the E.M.F. of one electrode only. What we have to measure, therefore, is the potential difference between the hydrogen electrode and another electrode of standard and known E.M.F. A suitable electrode to use in conjunction with the hydrogen electrode is the calomel electrode, which gives a standard E.M.F. which does not vary even with quite wide fluctuations of temperature or other similar factors. A typical form of the normal calomel electrode is shown in Fig. 6. At the bottom is a layer of mercury with a small length of platinum wire inserted into it for purposes of contact. Above this are a layer of a paste, made by mixing mercury with solid mercurous chloride, and a saturated solution of mercurous chloride in a normal solution of potassium chloride to maintain the concentration of chlorine ions, and therefore that of mercurous ions, constant.



In the saturated calomel electrode (Fig. 7) the mercurous chloride is dissolved in saturated potassium chloride solution, and *D* is a capillary tube which can be filled with saturated potassium chloride solution through the three-way tap *I* from the reservoir *R*. This capillary tube serves the purpose of making electrical contact between the calomel electrode and the solution under examination, in which the hydrogen electrode is immersed.

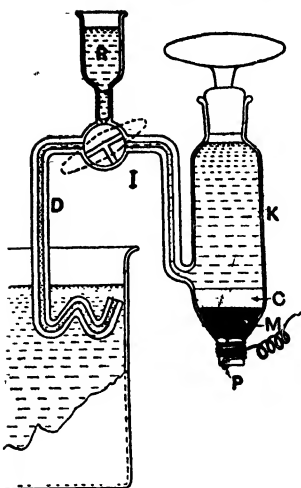


Fig. 7.—Saturated Calomel Electrode.

A cell may now be constructed with the calomel electrode as the positive pole and the hydrogen electrode as the negative pole, both being immersed in the liquid under examination. Such a cell is illustrated in Fig. 8, in which *W* is the liquid being examined, *H* the hydrogen electrode, and *K* the calomel electrode. The voltage of this cell is directly proportional to the pH-value of the solution, and is determined by the standard potentiometric method which is described in textbooks of physical chemistry.

*Glass Electrode.*—The hydrogen electrode suffers in practice from certain disadvantages, of which the most important are—

- (1) It is not convenient to use it for examining small quantities of liquid.
- (2) The electrode is easily poisoned by impurities, when it loses its sensitivity.

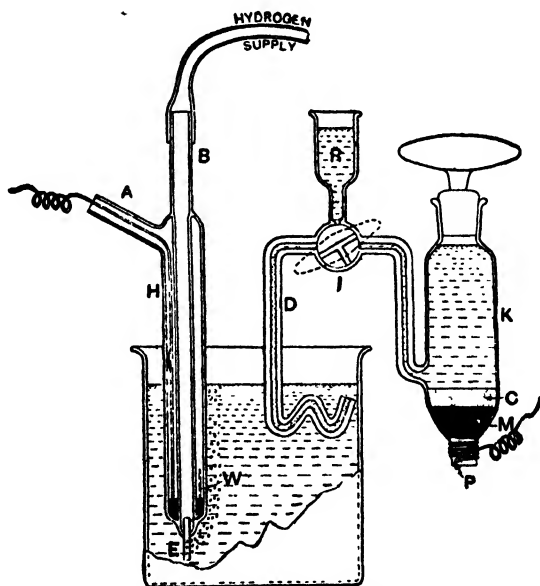


Fig. 8.—Complete Cell.

- (3) It is not always convenient to have a supply of gaseous hydrogen, especially when determinations must be carried out in the works away from the laboratory.

In modern apparatus, therefore, a glass electrode is used. This is constructed essentially of a very thin wall of glass (more recently it has been

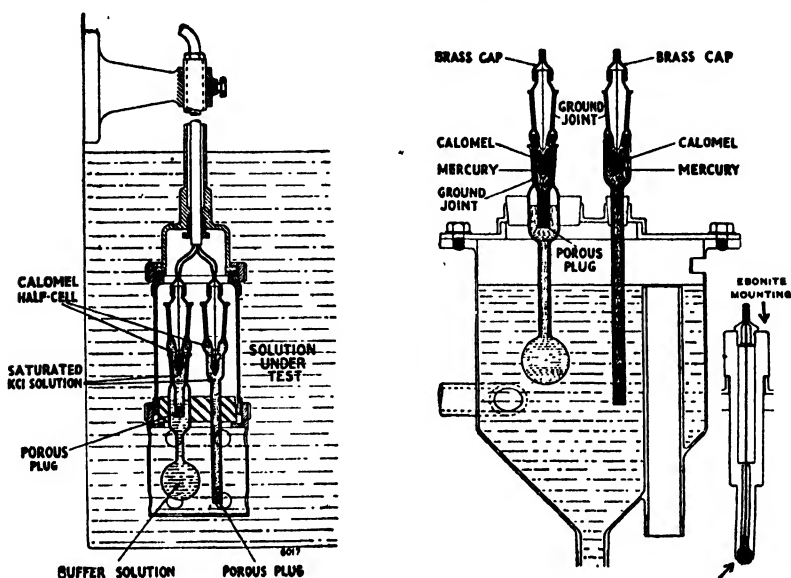


Fig. 9.—Glass Electrode.

possible to make these electrodes more robust by using thicker walls of specially selected glass), which separates two containers, into each of which is inserted a calomel electrode. A potential difference will be set up on either

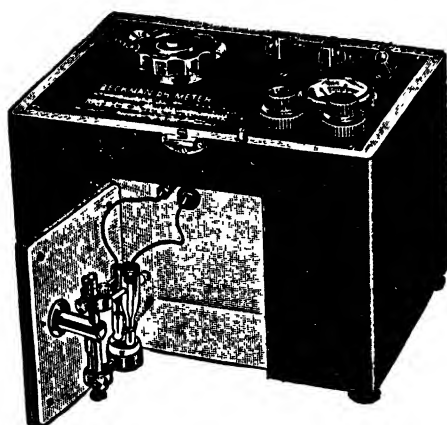


Fig. 10.—Self-contained *pH*-meter.

side of the glass membrane, proportional to the difference in *pH*-value between the two liquids. If the *pH* of one is known and constant, it is easy to calculate that of the other. A glass-electrode cell is illustrated in Fig. 9. Self-contained instruments, such as the apparatus shown in Fig. 10, which give direct readings of *pH*-values on calibrated scales, are obtainable.



### The Microscope.

The microscope has a place in textile technology which cannot be over-estimated. It affords a rapid method of detecting what fibres are used in the manufacture of any yarn or material. It is an invaluable instrument for giving clues regarding causes of damage. It is true that often they are only clues, subsequent confirmation with chemical tests being necessary. Much valuable time is saved, however, when the chemical tests to be carried out are confirmatory rather than exploratory. There are also certain common forms of damage, such as mildew, for example, which can be identified only with the aid of a microscope. For small magnification a simple microscope may be employed. Greater magnification is obtained with a compound microscope, the latter being the instrument which is commonly used.

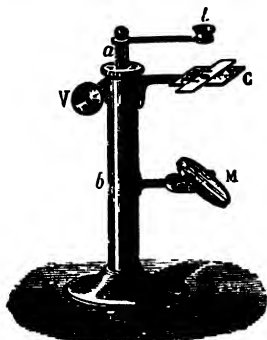


Fig. 11.—Simple Microscope.

**Simple Microscope.**—A simple microscope is shown in Fig. 11. It consists of a lens  $l$  of short focal length, mounted in a manner which permits of its being raised or lowered, and provided with a reflector  $M$  for illuminating the object to be examined. The lens is raised and lowered by means of the milled head  $V$ , which acts on the rack  $a$ .

**Compound Microscope.**—Although this is frequently a very delicate and elaborately constructed instrument, it always consists essentially of an objective, which corresponds to the lens  $l$  in the simple microscope, and an eyepiece, which further magnifies the already enlarged image given by the objective.

The mechanism of how a compound microscope produces magnification is shown in Fig. 12.  $ab$  is the object and  $O$  the objective, which is at the correct distance from the object to produce a clear image. The primary inverted image is seen at  $a_1b_1$ . This image is then viewed through the eyepiece  $O_1$ , which must also be in focus with respect to the primary image. This forms the final image  $AB$ . Fig. 13 shows a typical compound microscope.

**Objectives.**—Two or more objectives are provided, which may be screwed on to the nose-piece. These are generally made of a number of lenses according to the magnification required. As a rule, the greater the magnification aimed at, the more lenses are used in the construction of the objective. Different objectives are designated by their focal lengths—that is, the distance at which they must be placed from the object to give a clearly-defined image. Objectives commonly used are as follows.

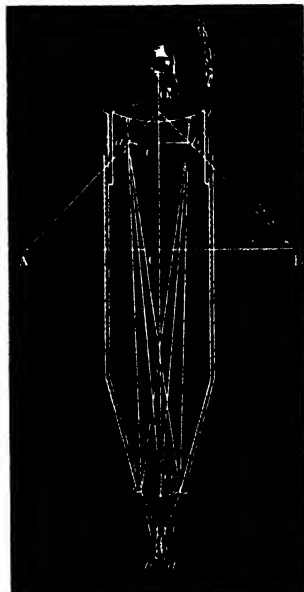


Fig. 12.—Compound microscope.  
Diagram of Images.

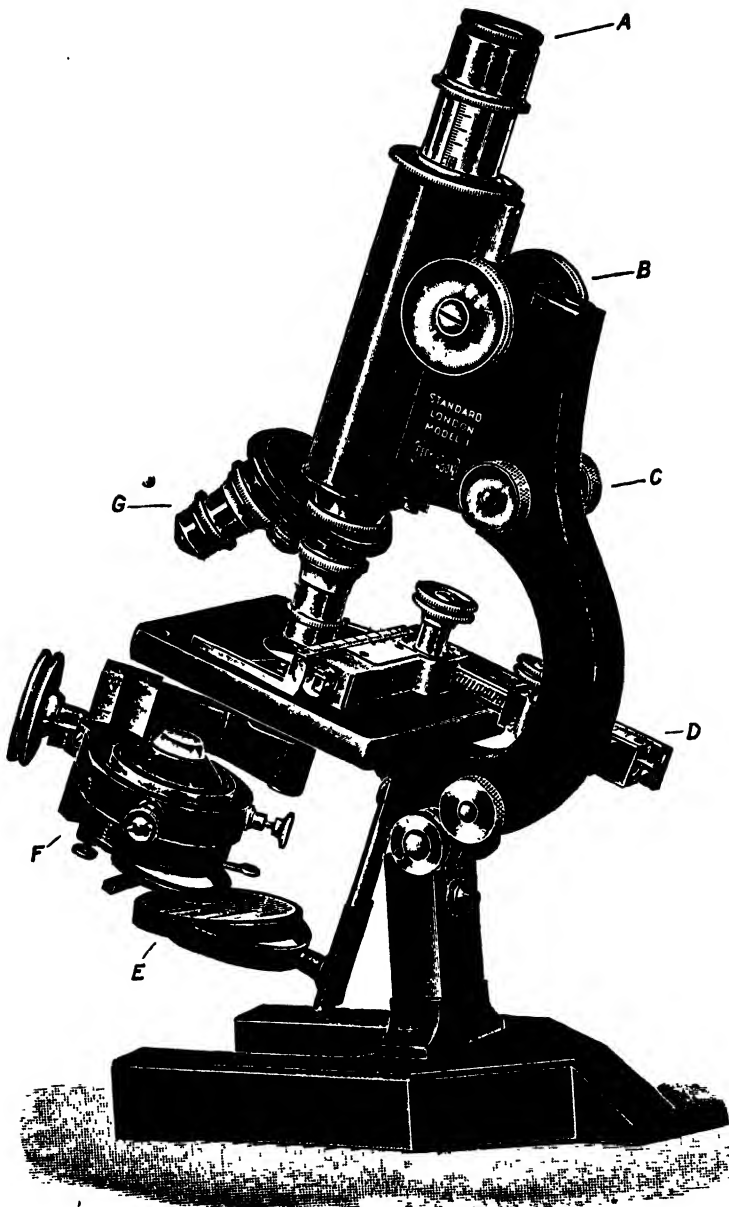


Fig. 13.—Compound Microscope.

A. Eyepiece.  
B. Coarse adjustment.

C. Fine adjustment.  
D. Travelling stage.

E. Mirror.  
F. Condenser.

G. Objective.

(1) The 1-inch objective, which gives a maximum field of view of 0.2 inch. It is especially useful for obtaining a general view of a specimen.

(2) The  $\frac{2}{3}$ -inch objective, which gives a maximum field of view of 0.08 inch. It is especially useful for searching over the object to find those particular parts which are worthy of closer inspection under the high-power objective.

(3) The  $\frac{1}{4}$ -inch objective has a maximum field of 0.02 inch, and is sufficiently powerful for examining the detailed structure of objects such as textile fibres, hairs, and mildews.

(4) The  $\frac{1}{12}$ -inch objective or *oil-immersion* objective. This gives the very highest magnification, and is generally used for bacterial work. It is too powerful for textile fibres, because the magnification is so great that the actual area under observation is too small. The  $\frac{1}{12}$ -inch objective is termed "oil-immersion" because it is necessary to place a drop of oil over the cover-glass and allow the lens to dip into the oil. If air intervenes, the light emerging from the upper surface of the cover-glass is spread out by refraction, and an insufficient number of rays enter the aperture. If the air space between the cover-slip and the aperture had the same optical properties as glass, this would not happen. Cedar-wood oil, however, has these properties. If the space between the cover-slip and the aperture is filled with this oil, it is equivalent to filling it with glass. With a  $\frac{1}{12}$ -inch objective, in which the actual aperture is very small, the effective aperture is increased by putting a drop of cedar-wood oil on the cover-slip and immersing the end of the objective in it.

**Magnifying Power.**—The magnifying power of a microscope denotes the size of the final image produced compared with that of the object when placed 10 inches from the eye. Generally the magnifications obtained with the various objectives are as follows:

Objective.	Magnification.
$\frac{1}{4}$ -inch . . . .	120 times
$\frac{1}{3}$ -inch . . . .	180 times
$\frac{1}{12}$ -inch . . . .	360 times

These figures are not absolute, because actually the magnification will depend on the eyepiece used.

Both object-glasses and eyepieces must be preserved carefully, particularly the latter. Scratches or dust scatter the light passing through, and any traces of grease cause an indistinct image to be formed. Lenses should never be touched with the fingers, since these leave grease on them. Dirt on the eyepiece shows in the field of view, whilst that on the objective does not, but makes the image indistinct. It can be detected in the eyepiece by revolving it in the draw-tube, when the specks also will rotate. If the specks are on the objective, or due to the eye of the observer, they remain stationary when the eyepiece is rotated.

The eyepiece can be cleaned with a piece of soft, well-washed silk, or if this does not remove the dirt, the silk should be moistened with xylol or alcohol. Objectives should never be taken to pieces. Any dirt is generally on the outer surface, and can be removed by wiping the surface gently with silk or chamois leather, avoiding scratching the glass. When not in use it is best to keep the objectives in the screw-cases provided for them.

An important factor with objectives is the thickness of the cover-glasses used. In the case of high-power objectives the effect of the thickness of the

glass is considerable. Low powers are not so much affected. As a general rule, whilst thick cover-glasses may be used with low-power objectives, only thin ones are suitable for the  $\frac{1}{4}$ -inch or higher-power objective.

**Illumination of Object.**—The object must be well illuminated before it can be examined. For this purpose a beam of light is directed through the object into the microscope by means of a mirror below the stage, which can be moved in all directions. The direction of the light should be such that it shines directly along the line which passes through the centre of the microscope, known as the *optical axis*. Oblique light prevents a clear image from being formed, and may produce an incorrect appearance.

The following method may be used to test whether the illumination is oblique: Where the light which illuminates the object is oblique instead of truly central, the object will not only become indistinct on either side of the focus, but will appear to move from side to side when it is put in and out of focus. If the light is central the object will become less distinct on either side of the focus, but will not alter its position.

The mirror can be used to make the light parallel, convergent, or divergent as desired. The flat side of the mirror gives light consisting of parallel rays if the source is at a considerable distance from it, whilst if the source of light is close to the mirror divergent light is produced. The concave side of the mirror gives convergent light. Light may be made still more convergent by means of a condenser fixed underneath the stage with an iris diaphragm (*F*, Fig. 13) beneath it. When the condenser is used, the flat side of the mirror is employed, since it will only deal with light which is parallel or slightly divergent. Although daylight is suitable for most purposes, artificial light is best for observing fine details with the aid of a condenser. When not required the condenser may be rotated so that it is out of the line of light from the mirror to the stage, as shown in Fig. 13.

**Focussing the Object.**—The illumination having been correctly arranged, the object must be brought into focus. The main body of the microscope carrying the lenses is carefully moved downwards by means of the rack and pinion used for coarse adjustment till the object begins to become apparent. When using high-powered objectives great care must be taken not to bring the objective right down on the glass and break the slide. The best way of proceeding is to start with the point of the objective nearly touching the cover-glass and work backwards until the object becomes visible, finally getting the exact focus by means of the fine adjustment.

**Mounting Specimens for Examination.**—It is a mistake to put too much of the specimen on the slide at once, because too much light will be obstructed.

Objects cannot, as a rule, be examined in the dry state. They must be mounted in some liquid medium, and in almost every case water is suitable. In the case of a powder such as starch, a little of the sample is thoroughly mixed with cold water, and a drop of the mixture placed on the slide. A cover-glass is then lowered carefully on to the drop in such a way as to avoid the formation of air-bubbles. Fibres such as wool are teased apart with two needles and wetted out thoroughly before mounting. When it is necessary to make out minute details of structure, greater transparency, although at the expense of clearness of outline, is obtained by mounting in glycerol instead of water.

When it is desired to keep a slide permanently for demonstration or as a standard of comparison, the specimens should be mounted in Canada balsam. This is a viscous liquid which sets to a solid on exposure.

Staining with solutions of dyestuffs may also be made use of to bring out details of structure.

**Measurement of Dimensions of Objects.**—Microscopic measurements are expressed by the symbol " $\mu$ ," which represents one thousandth part of a millimetre. For this purpose a micrometer eyepiece is used, or a glass engraved with a scale which can be inserted into an ordinary eyepiece. An alternative is to use a slide with very fine markings on it, against which the object can be measured.

**Photographic Records.**—In the examination of textile fibres or damaged goods permanent photographic records are often very useful. For this purpose a photo-micrographic apparatus is used. There are many elaborate types of apparatus available for extremely refined work, but the principles involved may



Fig. 14.—Camera Attachment for Microscope.

be described in connection with the relatively simple camera attachment shown in Fig. 14. The microscope eyepiece is inserted in the camera, and is then fitted in its place. After the plate has been inserted, the microscope is adjusted until a clear image of that portion of the slide to be photographed is seen through the eyepiece marked *C*. The centre of that part of the field to be recorded should be at the point of intersection of the crossed hair-lines in the lateral eyepiece. The image which is seen through this eyepiece is also projected on to the photographic plate, and the exposure may be made by operating the camera mechanism when the object is satisfactorily defined in the field of view.

**Fibre-diameter Measurement.**—The measurement of the diameters of textile fibres is often very important. In the case of wool it is frequently used as a means of assessing the quality of the sample under investigation. A special type of microscopic apparatus has been designed by the Wool Industries Research Association for rapidly and easily determining fibre-diameter. It consists of a projection microscope *L* (Fig. 15) which gives a projected image with a magnification of  $\times 500$ . The stage *S* carries glass slips, between which the fibres to be measured are mounted, and it is illuminated by a lamp *H*. The

slide-holder is adjustable in three directions: first, laterally, to bring any selected fibre into the field of view; second, transversely, to move this fibre along the field for variations of diameter to be observed; and thirdly there is a vertical movement for bringing any selected part of the fibre into view. The focussing is operated by movement of the stage and not of the objective, so that the magnification of the projected image will be constant. The transverse and focussing movements of the stage are operated by the control heads  $C_1$  and  $C_2$ . The image of the fibre is projected on to the screen  $T$ , where it may be measured with a transparent

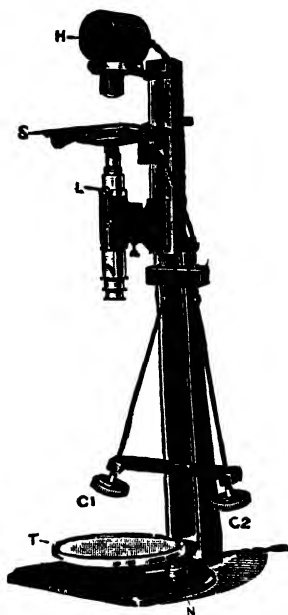


Fig. 15.—Apparatus for measuring Fibre-diameter.

celluloid ruler. An average of at least a hundred readings should be taken in determining the fibre-diameter of a sample. Obviously the measurements recorded on the transparent ruler must be divided by 500 (the magnification) to obtain the true fibre-diameter.

### Colour Measurement.

Dyeing is the production of colour on textile materials. Our ordinary language does not provide means of describing colours accurately. To say a material was "light red" means very little, and nobody could reproduce the shade exactly from such a description. The describer would find that his ordinary conversational vocabulary contained no words with which he could specify the colour so accurately that the dyer could match it without seeing a sample.

Colorimeters are instruments by means of which colour is described in terms of wavelengths of the light reflected.

**Bolton and Williams Colorimeter.**—This apparatus (Fig. 16) measures the light passing through standard screens with a photo-electric cell. Light from



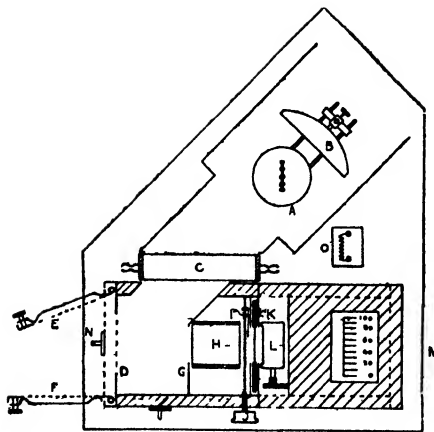
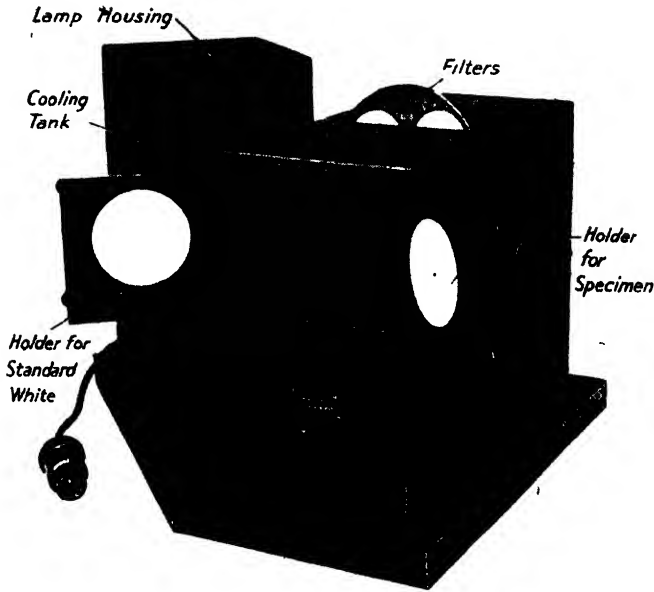


Fig. 16.—The Bolton and Williams Colorimeter.

the sample is reflected on to a photo-electric cell through nine standard filters of the following wavelengths:

460 m $\mu$ .	Blue	580 m $\mu$ .	Yellow
490 m $\mu$ .	Blue-green	610 m $\mu$ .	Orange
510 m $\mu$ .	Green	640 m $\mu$ .	Red
530 m $\mu$ .	Green	680 m $\mu$ .	Deep red
570 m $\mu$ .	Yellow-green		

A red shade reflects much red light and little at the blue end of the spectrum. The red rays pass through red filters but not through blue or green ones. A strong current will be set up in the cell, which will be accordingly registered on the galvanometer when the red filter is placed between the object and the cell. On the other hand the current will be only feeble when the blue filters are inserted.

The percentage reflections (calculated from the galvanometer deflections) with the various screens are given in Table IV and Fig. 17 for red and blue surfaces.

TABLE IV.—RESULTS OBTAINED WITH THE BOLTON AND WILLIAMS COLORIMETER.

Filter Wavelength, m $\mu$ .	Percentage Reflections with Red Fabric.	Percentage Reflections with Blue Fabric.
460	2	40
490	2	25
510	3	15
530	4	10
580	8	5
610	15	3
640	50	2
680	16	0

These wavelength curves give complete analyses and permanent records of colours.

A (Fig. 16) is the source of light, a powerful projector lamp. The rays from this lamp pass through a cooling tank through which cold water runs.

The coloured material to be tested is clipped into the holder *F*, and a standard white surface into the holder *E*. The reflected light is filtered through a 1 per cent. copper sulphate solution contained in the cell *H* in order to remove all infra-red rays from the light.

The colour screens are next inserted at *K*, and the rays then fall on the photo-electric cell, which is connected with a galvanometer, the scale of which is shown at *M*. This scale is calibrated so that it registers the percentage reflection of light directly.

Before each reading with a coloured screen the pure white surface is inserted, and the galvanometer is reset with the mechanism adjusted so that it shows 100 per cent. reflection from the standard white surface.

**The Donaldson Colorimeter.**—This was designed by the National Physical Laboratory and made by Adam Hilger Ltd., and is the apparatus most commonly used for research work or refined colour-measurement. The light reflected by or transmitted through the sample under investigation is compared with that produced by mixing varying proportions of the primary colours.

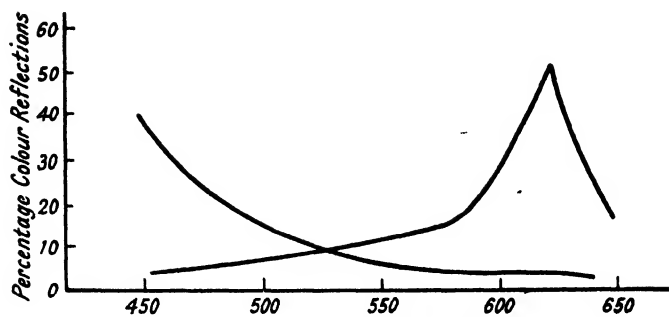


Fig. 17.—Wavelength Curves for Coloured Fabrics.

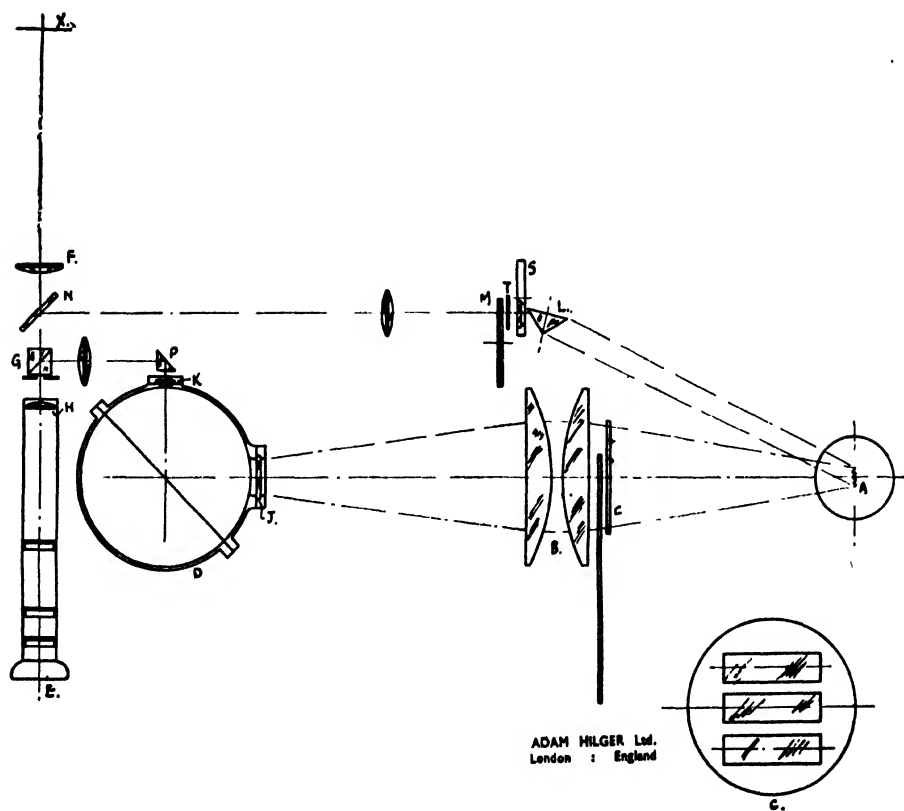


Fig. 18.—The Donaldson Colorimeter.

The principle of this colorimeter is shown diagrammatically in Fig. 18. Light from the lamp at *A* passes through three primary colour-filters *C*. The beams pass into a spherical colour-mixing chamber at *J*, from which the rays, thoroughly mixed, emerge at *K*. This beam is deflected through a photometric cube *G* so that it illuminates half of the field at the eyepiece *E*. The other half of the field is filled with light from the specimen at *X*. The shutters at *C* are adjusted by calibrated knobs, which record the amount of each of the primary colours admitted. These knobs are moved until the light passing through the screens matches the rays reflected from or transmitted through the sample. The colour is measured by the recordings of the proportions of primary colours needed to give a match.

When the colour of the sample is very highly saturated some measure of desaturation is desirable. This can be achieved by passing some of the light from the lamp *A* through the prism *L* and mixing it with the light from the specimen by means of the transparent reflector *N*. This light may pass through one of three colour-filters (identical with the three filters used at *C*) mounted on a rotating wheel *S*, or, alternatively, through a fourth filter approximately correcting the composition of the admixed light to daylight. The intensity of this desaturating light is varied by means of a circular neutral-tint optical wedge *M*.<sup>1</sup>

**The Lovibond tintometer** is described in Chapter XXXVI.

<sup>1</sup> We are indebted to Adam Hilger Ltd. for this description of the apparatus.

## CHAPTER IV.

### MICRO-ORGANISMS, ENZYMES, AND COLLOIDS.

**MICRO-ORGANISMS** play an important part in the textile industries. The atmosphere, water—and, in fact, every natural substance which does not of itself inhibit their growth—are always contaminated with micro-organisms. Raw cotton, for example, may contain from 1 to 100 millions per gram. The term “micro-organism,” in its widest sense, denotes any living organism, of either animal or vegetable nature, which is invisible to the naked eye, but its use is generally limited to those known as (1) bacteria, (2) moulds, and (3) yeasts.

**Bacteria** consist of small, unbranched vegetable cells. Each cell is composed of a minute quantity of vegetable protoplasm surrounded by an envelope

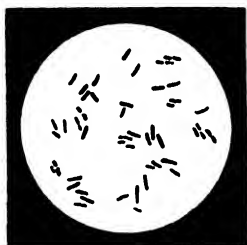


Fig. 19.—Bacilli.

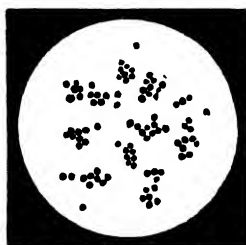


Fig. 20.—Cocci.

or cell-wall, which generally consists of cellulose. They are divided into two classes according to their shape, viz. (1) *bacilli*, or cylindrical rod-like forms; (2) *cocci*, which are rounded or spherical in shape. Figs. 19 and 20 show the appearance under the microscope of these two types, magnified 1000 times.

Bacteria vary in size. Cocci are the smallest forms, being seldom more than  $1/25000$  of an inch in diameter. Bacilli vary in length from  $1/12000$  to  $1/6000$  of an inch, their diameter being about the same as that of a coccus. Some bacteria are motile, propelling themselves in a liquid medium either by wave-like movements or by means of flagella. They may be either colourless or coloured. They are generally killed by steam or boiling water (though the spores may survive this treatment), and also by the action of certain chemicals, such as formaldehyde, which are termed *antiseptics*.

When dried at a low temperature, or kept at a temperature not exceeding  $0^{\circ}\text{C}$ ., bacteria are not killed, but their growth is inhibited. A certain amount of warmth is necessary for their propagation. Other essential conditions are the presence of moisture and food. Some bacteria require also oxygen and do not grow in the absence of air: these are termed *aerobic*. Some, called

*anaerobic*, grow in the absence of air, while others can flourish under either aerobic or anaerobic conditions. The food must contain nitrogen, salts, and, in fact, all the elements necessary to build up protoplasm and the cell-wall. Not only must the necessary elements be present in the food, but they must also be in a soluble and diffusible form. If they are not, the organism must be capable of bringing about these conditions, by means of bodies termed *enzymes*, which it secretes for the purpose. The medium must have also a certain reaction. Some micro-organisms cannot grow in the presence of acids, while others are either killed or their growth is inhibited by alkalis. In all cases there are distinct limits of alkalinity or acidity outside which the organism cannot develop. This is expressed in more scientific terms by saying that certain limits of *pH*-value (*i.e.* hydrogen- or hydroxyl-ion concentration) are favourable to their growth. The most important function of a bacterium is to reproduce itself. Under suitable conditions, it does this with marvellous rapidity. If a sterilized solid nutrient material, such as a jelly made from gelatin, is exposed to the air, small opaque spots, or patches, will soon appear on its surface. Each of these consists of innumerable bacteria all derived, probably, from one individual which settled on to the surface of the jelly from the air. Each of these spots or patches is termed a *colony*. The reproduction of bacteria takes place in two ways: (1) by fission, (2) by spore-formation. The simpler and more common method is by fission. A membrane or partition makes its appearance and grows transversely across the cell, thus dividing it into two smaller cells or rods. These then separate, each being a new bacterium, which quickly becomes mature and repeats the same operation. In this way a single bacterium may produce many millions in a very short time, since the rate of production of new individuals is in the nature of a geometrical progression.

In the second method, a portion of the cell contents becomes surrounded by a wall or envelope. The enclosed portion then becomes granular in appearance, changing ultimately into a number of minute spores, each of which is enclosed in a hard, resistant coat. The original cell now disintegrates completely, thus liberating the spores. Each of these is capable of growing into a bacterium under suitable conditions, though it may be dormant for long periods without being harmed or losing its power of growth. Spores are much more difficult to kill than normal bacteria. The latter are all killed by boiling with water for a minute. Spores, on the contrary, can in some cases be boiled in water for half an hour without losing their vitality. Anthrax, or wool-sorters' disease, is propagated chiefly by spores, which survive ordinary processes of sterilization applied to the skins or wool. They do not develop until the necessary warmth, moisture, and food are available. They may lie dormant in dry wool or dust for an indefinite period, but as soon as the conditions favourable to their growth, such as introduction into the human body, are present they begin to develop at once into the bacteria from which they were derived, and which are the cause of anthrax.

*Examples of Bacteria.*—(1) *Bacillus subtilis* is a very common bacterium. It is present in air and water, and is always found in hay and straw. Since it is the only spore-forming organism present in hay, a pure culture of it may easily be obtained. An infusion of hay is made with water. This is heated in a flask at a temperature of 80° C. for about twenty minutes. All the bacteria present are killed, but the spores survive. If the mouth of the flask be now closed with a plug of sterile cotton-wool and the flask kept at a temperature of about 20° C. for two or three days, a pure culture of *Bacillus subtilis* will be obtained. If a drop of the culture be mounted on a microscope slide and

examined with an oil-immersion objective, the bacilli will be seen (Fig. 21). They are rather long rods with rounded ends, and are often joined together end to end, forming long threads. Individual bacilli will be seen to be motile, having a wobbling kind of movement, and by special methods of staining the flagella may be made visible (Fig. 22). When *Bacillus subtilis* is grown upon gelatin the latter is decomposed and becomes liquefied.

*Bacillus subtilis* reproduces itself by both fission and spore-formation. The spores are extremely resistant, and can withstand a dry heat of 120° C. for an hour without being killed.

(2) *Bacterium prodigiosum*, which occurs in air and water, is a non-motile form which does not produce spores. It grows rapidly on such materials as gelatin and starch, causing their liquefaction. As it grows it produces a red

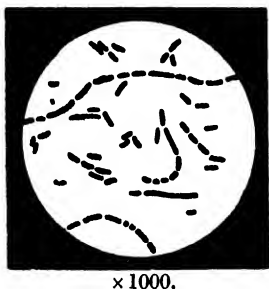


Fig. 21.—*B. subtilis*.



Fig. 22.—*B. subtilis*, showing Flagella.

colouring matter, although the bacteria themselves are colourless. This colouring matter is the cause of "bleeding" bread.

(3) *Bacterium fluorescens liquefaciens*, also found in impure water, together with others of a similar nature, causes the liquefaction of such nutrient media as gelatin, with the production of a disagreeable putrefactive odour.

(4) *Lactic-acid bacteria* and *Bacillus saccharobutyricus* are common organisms whose growth is accompanied by the production of acids.

**Moulds.**—If a moist organic substance, which contains suitable food materials such as starch paste, is exposed to the air it generally becomes covered with a white or coloured silky growth known as *mildew* or *mould*. Moulds belong to a class of vegetable organisms termed *fungi*, and are plants of very simple structure. If some mildew is examined under the microscope it is seen to consist of a mass of fine filaments, which are known as *hyphæ* (Fig. 23), and make up the body of the plant. The ramifying mass of hyphæ is termed a *mycelium*.

No division into cells can be observed, the whole organism being a branched filamentous cell containing the cell substance or protoplasm. At first the growth is confined to the mycelium, but after a time vertical hyphæ also are produced, each of which ends in a rounded capsule called a *sporangium*. The sporangium soon becomes divided off from the hypha by a transverse partition, and the protoplasm within it then becomes changed into a number of spores, separated from each other by a gelatinous substance which swells up under the influence of moisture. When the spores are matured the swelling of this substance causes the sporangium to be ruptured and they are set free. When the spores are exposed to suitable conditions they germinate and reproduce the mould. But moulds can also reproduce themselves in another way, namely, by a process termed *conjugation*. Two short club-shaped hyphæ

grow out from two adjacent ones till they touch each other. In each of these a cell-wall is formed, cutting off the contiguous portions from the remainder. Then the cell-wall between the two touching hyphæ disappears, and the two portions cut off by the partitions fuse together and form a new cell termed a *zygospore*. This separates from the rest of the plant, and germinates under favourable conditions. When it does so, it becomes ruptured, and an unbranched hypha grows out. At the end of this a sporangium is formed, filled with spores which are set free in the usual way. The description given refers to a common mould, *Mucor mucedo*. The life-history of others is very similar.

**Yeasts.**—There are a great many kinds of yeast. Some are made use of in brewing, owing to their power of converting dextrose or maltose into alcohol



Fig. 23.—Mould.

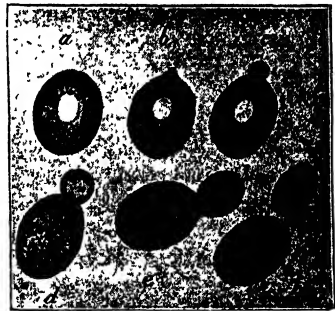


Fig. 24.—Yeast Cells.

when grown in a solution containing food material and these bodies. Carbon dioxide is produced at the same time. Others, termed *wild yeasts*, present in the atmosphere, although they produce alcohol, *i.e.* cause fermentation, give rise to bodies of an objectionable nature at the same time. A very similar kind of organism, namely, *Torulopsis*, sometimes produces threads resembling the hyphæ of a mould and often coloured growths. This is the case with "black" and "pink" *Torula*. The yeast plant consists of a single rounded or elliptical cell, with a somewhat thick cellulose coat or cell-wall (Fig. 24).

The cell contains protoplasm which is more or less granular in appearance according to the age of the cell. The protoplasm is permeated by a cell liquid which collects in places, forming one or more *vacuoles*. Yeast reproduces itself commonly by *budding*. A small end or excrescence is pushed out from the surface of the cell. This grows till it is nearly as large as the original cell, when it detaches itself, forming a new individual. In the absence of sufficient food, yeast reproduces itself by spore-formation in the same way as bacteria. If the lower end of a small block of plaster of Paris be immersed in water, some yeast placed on the top, and the block kept at a temperature of about 25° C. for a few days in a damp chamber, budding will cease. The protoplasm of the cell becomes granular and is changed gradually into spores, each surrounded by a coat of cellulose. The cell then bursts, liberating the spores, each of which is capable of producing a new yeast cell.



**Products of the Growth of Micro-organisms.**—The products of the growth of micro-organisms are of great importance in textile trades. The chief of these may be mentioned.

(1) Many are *chromogenic*, i.e. produce colour. Coloured spots or diffuse patches on goods may be due to colonies of moulds, bacteria, or *Torulopsis*. An interesting example of this was examined by the authors. A number of pieces of white lace developed, on storing, a pink colour, which was so evenly distributed that the goods appeared almost as if they had been dyed. Microscopic examination showed that innumerable hyphæ were interlaced with the cotton fibres. Cultivation of these on a sterilized starch medium proved the presence of a chromogenic mould capable of producing the pink colour observed when grown on sterilized cotton.

(2) When bacteria or other organisms grow upon or in a nutrient medium they generally cause complicated chemical changes to take place in the medium. Some, for example, cause the liquefaction of gelatin. Others change starch into soluble starch or even into sugars and acids. In order that food may be made use of by vegetable cells it must be soluble in water and diffusible. Hence, when a micro-organism grows on an insoluble and indiffusible substance, like starch-paste or gelatin, it must first convert it into soluble and diffusible compounds, which are also simpler in structure. In order to do this the cell secretes a body termed an *enzyme* or *ferment*. This acts as a catalytic agent, i.e. it can bring about a chemical change without itself being altered.

(3) Sometimes the products of the growth of micro-organisms or of the decomposition of the nutrient medium have an objectionable odour. The growth of mildew is generally accompanied by a peculiar musty smell. Sulphuretted hydrogen and other gases are also produced in the same way.

(4) Textile fibres, especially if incompletely cleansed and damp, serve as food for micro-organisms. When attacked they are gradually destroyed, causing "tenderness." For example, *Bacillus subtilis* can destroy wool completely, while other bacteria (e.g. *Bacillus cella-resolvens*) can disintegrate cotton. Bacteria are made use of in the retting of flax to disintegrate or soften the cortex of the plant.

(5) Many bacteria when they grow produce poisons or toxins, though these are not primarily of importance in textile operations. The diphtheria bacillus, for example, secretes a poison which frequently causes the disease to be fatal.

**Causes of Infection by Micro-organisms.**—Textile fibres or fabrics may become infected at almost any stage of their manufacture. A few of the principal causes are as follows:

(1) The use of polluted water. Impure water nearly always contains putrefactive, liquefying, and chromogenic organisms, as well as spore-forming bacteria such as *Bacillus subtilis*.

(2) Want of cleanliness in plant and buildings. Dust and dirt always contain bacteria. Accumulations of dust should be avoided, apparatus frequently cleaned, and the walls and ceilings of buildings often lime-washed.

(3) Letting goods lie about in a damp condition, especially in warm weather. Warmth, moisture, and absence of light favour the growth of any micro-organisms which may be present in the goods.

(4) Careless storing of finished goods. The atmosphere should be dry and not too warm. For example, if cotton goods contain more than 9 per cent. of water any micro-organisms which are present multiply rapidly. With a water content below 9 per cent. multiplication does not take place.

(5) The use of low-grade materials in finishing. Thus, a damp starch will

probably contain mould, whilst low-grade glues or gelatins are very liable to be attacked by liquefying and putrefactive organisms.

**Methods of Destroying and Inhibiting the Growth of Micro-organisms.**—Moulds and bacteria may be destroyed by means of dry or moist heat, diffuse sunlight, and chemical reagents. Nearly all bacteria are killed by exposure for a few minutes to moist steam at 100° C. Spores require a much longer time. Dry heat is not so effective. A temperature of 140° C. is necessary to kill bacteria, while spores can withstand even this treatment for some time, a temperature of 150° C. being necessary to kill them. Diffuse sunlight has a powerful inhibiting effect upon the growth of nearly all kinds of bacteria. This action is attributed to the ultra-violet rays. In some cases germs are completely killed by sunlight. This is the principle of the process of hanging clothes out in the sun to disinfect them.

Chemical substances which exert an inhibiting or toxic action on bacteria are called antiseptics, or disinfectants. Those which merely retard or inhibit growth are *antiseptics*, while those which kill bacteria and their spores are called *disinfectants*. There is no definite distinction between the two, since many are antiseptics when used in small and disinfectants in larger quantities.

The following bodies are used as antiseptics (or preservatives) or disinfectants: bleaching powder, sulphurous acid, carbolic acid, benzoic acid or sodium benzoate, salicylic acid, boric acid and borax, formaldehyde, salts of copper and zinc. The quantity required to inhibit bacterial growth varies with the substance used. The percentages of some common preservatives necessary to preserve starch paste are as follows: zinc chloride, 5–6 per cent.; boric acid, 2 per cent.; copper sulphate, 0.5 per cent.; salicylic acid, 0.5 per cent.; phenol, 0.3 per cent.

*Shirlan*.—The Cotton Research Association has developed a product termed “Shirlan” which is used extensively to prevent the growth of mildew in textile materials. It is salicylanilide and is soluble in ammonia or other mild alkali. In such solutions it has a direct affinity for cotton, and it may be applied at any stage of manufacture.

### Enzymes.

It has been stated above that bacterial growth is accompanied by chemical changes in the nutrient medium, and that these changes are due generally to the action of an enzyme or ferment secreted by the bacterium. These are found also in animal and vegetable tissues. Most of the chemical changes connected with life are due to the action of enzymes. The digestion of food is an example. In seeds the reserve food-material such as starch is changed, when the seed germinates, into soluble and diffusible sugar by means of an enzyme secreted for this purpose. The action of an enzyme is somewhat similar to that of an inorganic catalytic agent, but differs in one respect, namely, that a definite quantity of the enzyme cannot induce an indefinite amount of chemical change; further, it acts only under certain specific conditions, such as hydrogen-ion concentration, temperature, and the presence of electrolytes.

Enzymes are colloidal organic substances giving the general reactions of proteins and containing a small amount of mineral matter. They are soluble in water but insoluble in alcohol and other organic solvents. Like proteins they are precipitated from their aqueous solutions by saturating them with sodium sulphate or ammonium sulphate. They are adsorbed from their aqueous solutions by salts such as calcium phosphate, and also by cellulose. They are destroyed at 100° C.; in many cases at a much lower temperature.

Every enzyme has a definite range of temperature at which it is active. At temperatures below the lower limit its action is slow, at those above the upper limit the action ceases and the enzyme is destroyed. Thus diastase, which occurs in malt, acts rapidly at 60° C.; at 70° C. the action is restricted, and at 80° C. it ceases. There are also particular limits of hydrogen-ion concentration between which each enzyme acts, some being active on the acid side, others on the alkaline side, of neutrality. Their action is not inhibited by the presence of many antiseptics, such as toluene, chloroform, and thymol, and these are often added to their aqueous solutions to prevent bacterial growth. It may be noted that what is usually termed an "enzyme" may consist of more than one specific entity, each contributing its share to the final result of their action. These are known as *co-ordinated enzymes*.

**Preparation of Enzymes.**—The material containing the enzyme is extracted with cold water or a dilute aqueous solution of glycerol. After settling, the clear liquid is concentrated at a low temperature under reduced pressure, then treated with excess of alcohol, and allowed to stand for several hours. The precipitate is separated, redissolved in water, and again precipitated with excess of alcohol. The precipitate is then separated and dried at a low temperature or *in vacuo*.

**Chemical Changes promoted by Enzymes.**—These are (1) hydrolysis, (2) oxidation, (3) reduction, (4) clotting of liquids, and (5) specific chemical changes. Hydrolysing enzymes may be divided into the following groups: (1) amylolytic, (2) proteolytic, (3) lipolytic, and (4) hydrolytic. Amylolytic enzymes change starch into sugars; proteolytic enzymes convert proteins into proteoses, peptones, and amino acids; lipolytic enzymes split fats into fatty acids and glycerol, whilst hydrolytic enzymes bring about hydrolyses, such as changing cellulose into dextrose.

In a few cases a special chemical reaction is induced, such as the formation by zymase of alcohol and carbon dioxide from dextrose.

The chief common enzymes, together with their uses, are given in Table V.

**Use of Enzymes in Textile Processes.**—Diastase has important uses in textile processes. It is used firstly to remove starch from cotton goods and secondly to prepare mixtures of starch, soluble starch, and dextrin employed in the finishing of cotton goods. Commercial preparations of malt-diastase are made by extracting germinating barley with cold water, filtering, and concentrating. The filtrate is evaporated *in vacuo* until it has a specific gravity of about 50° Tw. Malt-diastase acts slowly at atmospheric temperatures, but rapidly at 60° to 65° C. The goods are digested with water containing the diastase preparation until no blue colour is produced with iodine solution. It is essential that no alkali should be present—that is, the pH of the liquid must be approximately 7.0. "Rapidase" is prepared from a culture of *Bacillus subtilis*. It can be used in either a neutral or a faintly alkaline medium (pH 8) and at a much higher temperature than diastase. At 80° to 85° C. it requires only a few minutes to free goods from starch. When diastase acts on starch, the proportion of dextrin produced depends upon the proportion of diastase present and the temperature of the reaction. By varying the proportion of diastase and regulating the temperature of the reaction the composition of the product can be controlled. When only a small proportion of diastase is present and the temperature is not above 65° C., the conversion of soluble starch into maltose and dextrin is comparatively slow, and may be represented by the equation:

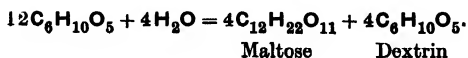
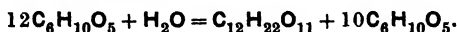


TABLE V.—SOURCES AND PROPERTIES OF ENZYMES.

Enzyme.	Source.	Temperature of Action, ° C.	Reaction of Medium.	Process.
(1) <i>Amylolytic.</i> Diastase . . . Amylase . . . "Rapidase" . .	Malt Saliva <i>B. subtilis</i>	60-70 37 80	Neutral Neutral Neutral or faintly alkaline	Starch → soluble starch → maltose + dextrin. Starch → soluble starch → dextrose. Starch → soluble starch → maltose + dextrin.
(2) <i>Proteolytic.</i> Pepsin . . . Trypsin . . .	Stomach Pancreas	37 37	Faintly acid Faintly alkaline	Protein → peptone → amino acid. Protein → peptone → amino acid.
(3) <i>Lipolytic.</i> Lipase . . .	Castor oil and other seeds, pancreas	20-30	Neutral	Fat → fatty acid + glycerol.
(4) <i>Hydrolytic.</i> Emulsin . . . Maltase . . . Cellulase, cytase Pectase . . .	Bitter almonds Yeast Water, etc. Fruits	15-25 60-70 15-25 15-25	Neutral Neutral Neutral Neutral or faintly acid	Amygdalin → glucose + benzaldehyde. Maltose → dextrose. Cellulose → soluble cellulose → dextrose. Pectose → pectin → pectic acid.
(5) <i>Oxidizing.</i> Catalase . . . Bacterium aceti	Malt Mother of vinegar	15-25 15-25	Neutral Acid	Oxidation of organic matter. Alcohol → aldehyde → acetic acid.
(6) <i>Reducing.</i> Reductase . .	Milk, sewage, bran	15-25	Faintly acid to faintly alkaline	$\text{SO}_4^{--} \rightarrow \text{H}_2\text{S}$ ; indigo → indigo white; methylene blue → leuco compound.
(7) <i>Clotting.</i> Rennin . . . Thrombase . .	Calf's stomach Blood	15-25 15-25	Neutral to faintly acid Neutral	Coagulation of milk. Coagulation of blood.
(8) <i>Special Reactions.</i> Zymase . . .	Yeast	15-25	Neutral or faintly acid	Dextrose → alcohol + carbon dioxide.

When a greater proportion of diastase is used and the temperature is above 65° C., conversion of soluble starch is rapid, and the proportion of dextrin increases, reaching a maximum at 70° C., the reaction at this temperature being represented by the equation :



By taking advantage of these facts, finishing mixtures can be made which contain the desired proportions of starch, soluble starch, and dextrin.

Proteolytic enzymes are used sometimes in the degumming of silk, whilst reductases are responsible for the reduction of indigo to indigo white when the fermentation process is used.

### Colloids and the Colloidal State.

Graham, in 1861, found that crystalline substances, both organic and inorganic, when dissolved in water, are able to diffuse through a parchment membrane. For these experiments he used an apparatus known as a dialyser (Fig. 25). This consists of a bell-shaped glass vessel open at both ends. The lower end is covered with a piece of parchment or cellophane held in place by a rubber band. The dialyser is then suspended in a dish containing water, and the solution to be tested is poured in through the upper opening, which is then closed with a plug of cotton wool. After standing for a few hours, the liquid in the dish is tested for the dissolved substance. Some substances pass through the



Fig. 25.—  
Dialyser.

membrane, while others, such as glue, starch and albumin, do not. Graham named these two classes "crystalloid" and "colloid" respectively. When a mixture of the two is placed in the dialyser, and the water in the dish renewed at intervals, the whole of the crystalloid substance can be removed, leaving the colloid in the dialyser. This process is used for the purification of colloidal bodies. Graham thought that all soluble substances were either crystalloids or colloids.

The term colloid is now used in a different sense from that postulated by Graham. It is known that there is no dividing line between crystalloids and colloids and that practically all bodies are capable of existing in the "colloid state," in which one substance, known as the "disperse phase," is distributed uniformly in the other, the dispersion medium or "continuous phase." When the particles of a substance having a diameter of 1 to 100  $\mu$  are distributed in a continuous phase, a colloidal solution results. This is also termed a "sol." But the readiness with which substances assume colloidal properties is not always the same. The following terms are used in connection with this:—

(1) *Hydrophilic* and *hydrophobic*: The former disperse readily with water whilst the latter do not. The terminations "-philic" and "-phobic" are derived from Greek words meaning "love" and "hate" respectively.

(2) *Lypophilic* and *lypophobic*: These have similar meanings for dispersion media other than water.

There are three types of the continuous phase, viz. mechanical suspensions, colloidal solutions, and molecular solutions.

The particles in a colloidal solution are usually charged with negative electricity, and the addition of a positively charged electrolyte causes precipitation or coagulation of the colloid.

There are two main types of colloidal sols, viz. (1) the Gelatin sol type, (2) the Gold sol type.

The formation of a gelatin sol is accompanied by considerable swelling; the sol has a greatly increased viscosity, and a large quantity of an electrolyte is required to cause coagulation. Very concentrated sols can be obtained which, in the case of gelatin or starch, are liquid when hot but set to a jelly (or gel) on cooling, this process being reversible.

The gold sol has a low viscosity; there is no swelling, and only low concentrations can be obtained. It is affected by a small quantity of an electrolyte and, when coagulated, granules are formed, the process being irreversible. The term "coagel" is used to denote this.

The gold type is known also as "suspensoid," since the dispersed particles are solid, whilst the gelatin sol is "emulsoid," it being assumed that the gelatin exists in liquid droplets dispersed in the water. An emulsion may be defined as a system in which globules of one liquid are dispersed in globules of another. These globules may have a diameter of only 500 m $\mu$ . They are usually charged with negative electricity and are coagulated by adding a positively charged electrolyte. When a hydrophilic colloid such as gelatin is added to a hydrophobic colloid the hydrophilic properties of the latter are increased. This is due probably to adsorption of the hydrophilic colloid, which forms a protective layer on the hydrophobic colloid. The gelatin is termed a "protective colloid." It is used in this way in textile processes as also are starch, dextrin and Iceland moss.

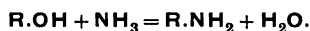
*Adsorption.*—The ability of colloids to form "adsorption compounds" is of importance in dyeing and other textile processes. This property is shared by such substances as charcoal and silica gel, which have a large surface. The difference between absorption and adsorption has been described by Slater (*J. Soc. Chem. Ind.*, 1925, **44**, 161). Substances in contact try to mix, and do so in many cases. When the molecules of two substances in contact with each other form a homogeneous mixture the process is termed *absorption*. Intermingling is often prevented by resistance to diffusion: the two substances can then only concentrate at the boundary surface in the attempt to mix with each other. This concentration of one substance at the surface separating it from another, producing a layer of increased concentration only a few molecules in thickness, is termed *adsorption*. Since adsorption is due to concentration of molecules at the surface of the adsorbent, it is natural that colloids, which have large surfaces, should behave in this manner. As a rule, adsorption is a reversible process. Thus, if charcoal be treated with a solution of acetic acid and filtered off, it will be found that acetic acid has been adsorbed; but if the charcoal be then washed with a more dilute solution of acetic acid, some of the acid will be removed, whilst repeated washing with water will remove all of it. For every concentration of acetic acid there is a definite proportion which is retained by the charcoal. The adsorbed substance may in some cases become changed by chemical action into another substance, thus leaving the exposed surface free to adsorb another layer of molecules. In such cases the process may be irreversible. This is what occurs in the process of dyeing wool with an acid dyestuff. The dye acid is first adsorbed at the surface, separating the wool from the dye liquor. It then combines with the basic groups of the wool protein, thus making the adsorption of more molecules of dye acid possible, these processes continuing until the dye-bath is exhausted. When silk is soaked in a solution of tannic acid a definite amount is adsorbed, depending upon the conditions, such as temperature and concentration of the solution. If this tannic acid is changed into an insoluble compound such as ferric tannate, the silk can again adsorb tannic acid, and by repeating these operations several times the silk can be heavily weighted.

## CHAPTER V.

### THEORIES OF DYEING.

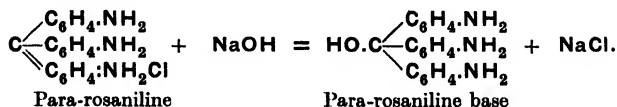
THE mechanism of the process by which dyes become permanently fixed on textile fibres is hard to understand and has caused much controversy. The theories which have been propounded fall into three classes, *viz.*: (1) chemical theories, (2) physical theories, and (3) electrochemical theories.

The chemical theories are the simplest, and perhaps the most feasible in many cases. The general idea is that the dyestuff undergoes chemical combination with the fibre. The combination may be the result of either a double decomposition or a reaction between the fibre and dissociation products of the dye. An important fact supporting the theories of this class is that cotton, which is not chemically reactive, has a direct affinity for only a very limited number of dyes, but wool and silk, which have both acid and basic properties, are directly dyed by the majority of dyestuffs. Vignon (*J. Soc. Chem. Ind.*, 1893, 12, 351) has made some interesting observations in connection with this fact. Heat is evolved when wool and silk are treated with acids, this indicating that chemical combination takes place. No heat is evolved when cotton is treated with acids, but when the fibre is treated with ammonia it becomes basic, and then combines chemically with acids. Ammonia probably converts the hydroxyl groups of cellulose to amino groups in the same way that it converts naphthol to naphthylamine:



Cotton which has been rendered basic differs from the original fibre in having a direct affinity for acid dyes.

When a basic dye is treated with an alkali the dye base is liberated, and a metallic chloride is formed:



Whilst the dyestuffs (*i.e.* the hydrochlorides) are coloured bodies, giving coloured solutions, the dye bases are colourless, and when soluble in water do not give coloured solutions. But these colourless solutions will dye wool or silk the same colour as the solution of the dyestuff itself. This is held to be evidence that the acid groups of the fibre have combined with the dye base to form a salt. It is known that when a dyestuff is dissolved in water it is partly split up or dissociated into its component parts or ions. Thus magenta, which is rosaniline hydrochloride, gives rise to rosaniline and chlorine ions. If the rosaniline ions remain in solution their number is limited,

but if they are removed as quickly as they are formed the dissociation will proceed till chlorine ions alone remain in solution. Knecht and Appleyard (*J. Soc. Dyers Col.*, 1888, 4, 72) found that when wool was allowed to exhaust a bath containing rosaniline hydrochloride, the liquor contained, at the end, an amount of ammonium chloride corresponding exactly to the hydrochloric acid in the rosaniline originally taken. This showed that the magenta-base ions had formed a compound or a salt with the fibre, and that ammonia had been simultaneously liberated. The latter, of course, would account for the ammonium chloride in the bath. This explanation has been extended to the dyeing of wool and silk with both acid and basic dyes. Many acid dyestuffs are split up or hydrolysed by water with liberation of dye acid, which, in turn, may form salts with the amino groups of the wool. The nature of the amino groups of wool, together with their function in the dyeing of this fibre, are discussed later.

Knecht has isolated an amphoteric substance called *lanuginic acid* from wool. This acid gives coloured and insoluble precipitates with acid and basic dyes. Though it is not known that lanuginic acid exists as such in the wool fibre, yet it is not improbable that it is formed in the dye-bath by the hydrolytic action of hot water or acid. A similar compound, known as *sericinic acid*, has been isolated from silk. Knecht has also shown that the quantity of dye taken up by the wool under certain circumstances is proportional to the molecular weight of the dyestuff. That hydrolytic action plays a part in dyeing has also been shown by the same author. When a drop of magenta solution is placed on a filter-paper it spreads rapidly. After a few minutes, however, a colourless halo appears round the coloured zone, which on examination is found to contain hydrochloric acid. A similar phenomenon is shown by Crystal Violet and methylene blue, but only to a small extent by malachite green. The appearance of a halo is an indication of hydrolytic dissociation, and addition of hydrochloric acid will prevent dissociation and, consequently, halo-formation. With acid dyes, such as picric acid, Naphthol Yellow, and Orange II, only a very small halo is formed, and that only at great dilution. Addition of acid to the solution, however, considerably increases the size of the halo. The interesting point is that it is found that the conditions which promote the formation of the ring are also those most suitable for dyeing with both acid and basic dyes. Thus in the case of basic dyes the presence of acid prevents dissociation, and also decreases the affinity of the fibre for dyes. Acid dyes, on the other hand, are dissociated to a greater extent in the presence of acids, and also dye wool and silk deeper under such conditions. It is known that there is a certain concentration of acid beyond which the addition of more has no effect on the affinity of wool for acid dyes. It is interesting to note that the same concentration of acid gives the maximum halo with acid dyes.

Willstätter (*Ber.*, 1904, 37, 3758) dyed wool with racemic mixtures of optically active dyes, hoping that one form would be taken up preferentially. The dye liquor, however, showed no tendency to become optically active during the dyeing. Gillet (*J. Soc. Chem. Ind.*, 1900, 19, 1105) made amyl alcohol feebly acid or basic by dissolving organic acids or bases in it. Such solutions, he thought, would be comparable with the animal fibres, and he therefore studied their behaviour towards solutions of acid and basic dyes. The behaviour of the amyl-alcohol solutions towards dyestuffs resembled that of the animal fibres.

The action of the acid in dye-baths in which acid dyes are used will be discussed in detail in the chapter devoted to these colours. It may be mentioned



here that it was once thought that the function of the acid was to liberate the dye acid, but the work of Speakman, which will be described later, has shown that other factors are concerned also.

**Physical Theories of Dyeing.**—There are objections to the chemical theories of dyeing, the most important of which is that cotton is such an inert substance from the chemical point of view that it is inconceivable that it should undergo any chemical reaction with the dye. One point of interest, however, is that when the hydroxyl groups of cotton are acetylated, as in cellulose-acetate silk, the affinity for direct dyes is almost entirely removed. This may, therefore, be taken as evidence that the hydroxyl groups of cotton play a part in substantive dyeing. It is also known that substances such as kaolin and glass beads, which could not possibly take part in a chemical reaction, can apparently be dyed in the same way as the textile fibres themselves. Hellot was one of the first to attribute dyeing to physical phenomena. He pointed out that the surfaces of the fibres are studded with pores, and these are probably of significance in dyeing. According to Hellot, the pores expand in a hot dye-bath, and allow the particles of dye to wander in. When the fibres cool the pores contract and imprison the particles. This theory is open to the obvious objection that the dye is not washed out by boiling water. Georgievics has been one of the strongest upholders of the physical theory of dyeing. He found that the ratio  $\sqrt{c_f/c_b}$  was constant, where  $c_f$  is the concentration of dyestuff in the fibre, and  $c_b$  the concentration in the liquor at the end of the dyeing operation. This equation points to physical rather than chemical causes. The solid-solution theory of O. N. Witt is interesting, in spite of the fact that it is not at present looked upon with much favour. Just as ether will remove benzoic acid from an aqueous solution of the latter, so will the textile fibre extract the dyestuff from the dye liquor. Dyeing depends, therefore, on the fact that the dye is more soluble in the fibre than in water, and the function of assistants is to decrease its solubility in water. When silk dyed with magenta is immersed in alcohol the colour is stripped off the fibre because it is more soluble in this solvent than in the fibre. When water is added to the alcohol, however, the dye goes on to the silk again because dilution of the alcohol decreases its solvent power for magenta. Witt also points out that magenta shows its characteristic colour only when in a state of solution, for the solid compound is green. Fluorescent dyes also show fluorescence only when in solution, and it is known that they show this phenomenon to a certain extent on textile fibres.

Colloids have received much attention in recent years, and it is inevitable that dyeing should be considered from this point of view. According to modern ideas the fibres themselves are colloidal, and it has also been found that many dyestuffs when dissolved in water give colloidal instead of true solutions. J. Müller (*J. Soc. Chem. Ind.*, 1904, 23, 747) says that the textile fibres are colloidal, and will dye only in the gel condition. This condition is induced by the action of water or acids in the case of wool and by alkalis in the case of cotton. Kraft (*J. Soc. Chem. Ind.*, 1899, 18, 757) attributes dyeing to the formation of a gelatinous colloidal membrane. Acid and basic dyes combine with the animal fibres forming such compounds. When the fibre is mordanted it is the mordant which combines with the dye to form the gelatinous membrane. Direct dyes are also coagulated on the cotton fibre. Dreaper (*J. Soc. Chem. Ind.*, 1905, 24, 223) states that dyeing is entirely a colloidal action, the function of assistants being to increase the state of aggregation of the dyestuff. He enumerates the following causes, all of which are contributory to the dyeing operation:—

(1) A solution state of the dye within certain limits of aggregation, as determined by the laws of size.

(2) A corresponding state of aggregation of the fibre.

(3) Effective localization of the dye in the fibre.

(4) Dissolution of dye, due to concentration effects of secondary attraction between the fibre substance and the dye.

(5) Indirect entrance of dye aggregates by molecular migration, with subsequent re-formation of aggregates within the fibre.

(6) Localization of assistants within the fibre.

(7) Dissociation in the case of basic dyes, leading to the formation of bases in a high state of aggregation.

(8) In some cases chemical combination may play a part. Bilz (*J. Soc. Chem. Ind.*, 1905, **24**, 920) found that the dyeing operation could be represented by the equation :

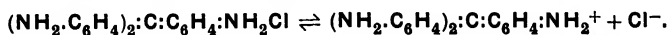
$$\frac{C_{\text{fibre}}^n}{C_{\text{dye liquor}}} = \text{constant.}$$

The same formula holds when inorganic colloids, such as aluminium hydroxide, take up dyes from aqueous solution, and hence dyeing is probably merely a case of adsorption. It is known that the particles of a colloidal solution are electrically charged, and Linder and Picton have shown that oppositely charged colloidal solutions will mutually precipitate each other. Colloidal solutions of dyestuffs also are precipitated by such solutions bearing an opposite charge, and the above authors think that this phenomenon plays a part in the dyeing process.

**Electrochemical Theory.**—Mention has already been made of the dissociation of dissolved dyestuffs in connection with the chemical theory. The products of this dissociation are electrically charged particles known as ions. Ponceau 4GB is the sodium salt of a sulphonic acid, and has the formula  $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3\text{Na}$ ; when dissolved in water it dissociates into an acidic ion,  $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3^-$ , which bears a negative charge, and a sodium (Na) ion, which bears a positive charge. Written in the form of an equation, this gives



In the case of basic dyes, such as para-roaniline  $[(\text{NH}_2\cdot\text{C}_6\text{H}_4)_2\cdot\text{C}:\text{C}_6\text{H}_4\cdot\text{NH}_2\text{Cl}]$ , the dye ion,  $(\text{NH}_2\cdot\text{C}_6\text{H}_4)_2\cdot\text{C}:\text{C}_6\text{H}_4\cdot\text{NH}_2$ , bears a positive charge, whilst the chlorine ion bears a negative charge:



The modern theories of dyeing depend on the fact that textile fibres when immersed in water take up a negative charge. The fibres would, therefore, be negatively charged when immersed in a neutral solution of a dyestuff. In a solution of a basic dye the fibre will naturally attract the oppositely charged dye ions, but in a solution of an acid dye the fibre would repel the similarly charged acid dye ion. It is well known that most of the acid dyes will not dye a fibre from a neutral solution. If the fibres be immersed in an acid solution their charge becomes changed from negative to positive, and they will now repel similarly charged basic ions but will attract the negative dye ions of an acid dye. This theoretical consideration is in accordance with facts, for every dyer knows that the addition of acid to a dye-bath will keep a basic dye off the fibre, but will drive an acid dye on to it.

This short summary of the numerous theories of dyeing will serve to show

that no definite solution to the problem has yet been found. The electrical theory accounts for the attraction of the dye to the fibre, but fails to explain satisfactorily how the dye is permanently fixed. It has been shown that there are serious objections to all the other theories. It appears that no general theory can be devised which will cover every case of dyeing. Modern opinion, however, seems to be fairly unanimously agreed upon the fact that the process consists of two stages. The first stage is the attraction of the dye to the fibre, probably by the process of adsorption, whilst the second consists in the permanent fixation of the dye on the fibre.

## CHAPTER VI.

### WATER.

A PLENTIFUL supply of good water is of the utmost importance in all textile operations in which it is used. Pure water is rarely obtainable; hence it is necessary to have a knowledge of the impurities which water is likely to contain and of the effects these will have in practice.

#### Classification of Natural Waters.

Waters may be classified as follows:

- (1) Rain waters, including all water derived directly from the atmosphere.
- (2) Surface water, that is, rain water which has been collected in lakes and streams.
- (3) Subsoil water, or water which has percolated into the subsoil and can be collected in shallow wells.
- (4) Deep-well waters, obtained from the deeper water-bearing strata, which are protected from the subsoil water by a comparatively impermeable stratum. This kind of water has generally travelled a long way through the earth, during which time natural purification has taken place.

**Rain water**, if collected in the open country, is the purest of all natural waters. It contains only the dissolved gases of the atmosphere, together with some finely divided solid matter derived from the air. Traces of ozone and hydrogen peroxide also are sometimes present. In the neighbourhood of towns it brings down with it dissolved and suspended impurities, such as soot, sulphuric acid, putrefying moulds, and bacteria. Hence it is only in open country districts that it can be used without treatment. It can be freed from its suspended impurities by filtration through a bed of fine sand. By making use of a proper storage tank, and adopting a suitable method of collection, it is often possible to obtain a fairly good supply of rain water. With an average annual rainfall of from 15 to 18 inches, about 150 gallons per week can be collected from 100 square yards of collecting surface. Although this is not a large quantity, it would be sufficient for some of the more delicate operations of bleaching or dyeing. If collected from a roof some method must be adopted by which the first portions are rejected, since these always contain dirt and other impurities. These first washings may be rejected by means of a canter balanced on a pivot. When it is full it overbalances, and discharges its contents into a waste pipe, after which the water runs direct to the storage tank. Collection from a roof could be largely supplemented by a gentle slope on the ground coated with cement.

A satisfactory filter can be made by filling a barrel or small tank with alternate layers of pebbles and fine sand, which naturally require renewing

periodically. Carefully collected and filtered rain water contains per 100,000 parts:

Total solids . . . . .	3.00 to 5.00
Sodium chloride . . . . .	0.01 to 1.00
Ammonia . . . . .	Trace to 0.025
Nitrates . . . . .	Trace.

Rain water, if not collected, trickles over the surface of the earth into streams, ponds, or lakes, or percolates into the soil. During this process it dissolves many bodies with which it comes in contact, and hence when it again becomes available for use it always contains impurities, many of which are objectionable in water which is to be used for bleaching or dyeing. The quantity and nature of these impurities vary with the nature of the strata through which the water has passed and the depth from which it is drawn. After rain water, speaking generally, the purest waters, from an organic point of view, are deep spring and well waters. These are followed by upland surface waters, moorland waters, river waters, subsoil waters, and shallow springs in the order named. Judged by mineral constituents, the order is not quite the same, the surface waters taking the first place, since the farther water percolates through the earth the greater is the opportunity for dissolving mineral matter.

**Surface Waters.**—As water passes over the surface of the earth it carries with it organic matter, in various stages of decomposition, both in suspension and in solution, and also dissolves more or less mineral matter, depending upon the nature of the soil and the slope of the watershed. When the water reaches a natural reservoir it deposits most of its suspended matter, but retains its dissolved organic and inorganic constituents. The dissolved organic matter is attacked by nitrifying bacteria in the presence of air, with the formation of nitrates. Thus, unless directly polluted by sewage, these waters are, as a rule, organically pure. They often receive considerable additions of dissolved saline bodies from shallow springs, bringing in water which has travelled some distance through the earth. Surface water has sometimes a distinct colour derived from the soil, and is generally saturated with air. Its character is variable. Where the surface is hard, impervious, and unable to support vegetation, the water runs off quickly and contains but little dissolved matter. When the rocks have become disintegrated by weathering, a certain amount of soluble matter is set free, and the débris becomes able to support vegetable life. In this way both organic and inorganic impurities are introduced into the water. If the surface is covered with peat or other decaying vegetable matter a large amount of organic impurities may be present in the water.

**Subsoil water** is obtained generally by means of shallow wells. Its quality is very variable, depending entirely upon the nature of the subsoil. It is often polluted with organic matter and contains, commonly, much saline matter. Its variable nature is seen from the following analyses:

	Parts per 100,000.			
	1.	2.	3.	4.
Total solids. . . . .	25.50	58.00	148.00	226.50
Sodium chloride . . . . .	3.44	10.80	7.68	25.00
Total hardness . . . . .	14.25	35.00	69.00	115.50

**Deep-well Water.**—Deep wells are those bored through the subsoil into the water-bearing strata beneath. If all subsoil water is excluded from the well,

these waters are generally free from organic pollution, but the mineral constituents may be so great in quantity as to render them unsuitable for bleaching or dyeing without preliminary treatment.

**Impurities present in Water.**—These are of two kinds, namely (1) suspended matter, and (2) dissolved impurities. The suspended matter includes finely divided particles of insoluble mineral matter; also organic matter of vegetable or animal origin, the former including micro-organisms such as bacteria. The coarser kinds of suspended matter can be removed by either sedimentation or filtration, but bacteria are so small that they pass through ordinary filter-beds such as those composed of sand.

**The dissolved impurities** cannot be removed by filtration. They include (1) soluble organic matter, (2) compounds containing nitrogen, including soluble organic substances, salts of ammonium, nitrates, and nitrites; (3) chloride and sulphate of sodium; (4) salts of iron; (5) salts of calcium and magnesium, which produce "hardness"; (6) dissolved gases.

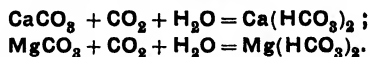
Soluble organic matter, nitrogenous organic compounds, ammonium salts, nitrates, and nitrites may be derived from either vegetable or animal matter. If present in considerable quantities they often indicate sewage pollution. Water containing sewage is unsuitable for any textile purpose, both on account of the dissolved impurities and also because it contains putrefactive or chromogenic micro-organisms, which would damage either the fabrics or the dressings used in finishing them.

Chlorides, present generally as sodium chloride, may be derived either from sewage or from the strata through which the water has passed. If sodium chloride is present in any quantity it gives goods a damp feel when finished. Sodium sulphate, which is often found in subsoil waters, acts in the same way.

Iron is commonly introduced by sewage pollution. Ferruginous water is unsuitable for use in either bleaching or dyeing. Dissolved gases, derived from the atmosphere, are always present. These include oxygen, nitrogen, and carbon dioxide. Oxygen is the most important. Water at 0° C. and 760 mm. pressure can dissolve 7 cc. of oxygen per litre, or one part by weight per 100,000. Dissolved oxygen must be removed for certain purposes such as indigo dyeing, and for boiler feed water. If oxygen is present in water used in boilers it always causes corrosion of the plates.

**Compounds of Calcium and Magnesium.**—These, which give rise to hardness, are the most important impurities from a textile point of view. Calcium and magnesium are commonly present in two forms: (1) bicarbonates, and (2) sulphates and chlorides. Bicarbonates produce "temporary" hardness, sulphates or chlorides "permanent" hardness.

**Temporary Hardness.**—The carbonates of calcium and magnesium are almost insoluble in pure water. Natural water always contains dissolved carbon dioxide. When water containing carbon dioxide acts upon calcium or magnesium carbonate a soluble bicarbonate is formed:



Thus water containing carbon dioxide dissolves calcium and magnesium carbonates from the rocks with which it comes in contact, and becomes hard. If this water is boiled the bicarbonate is decomposed into carbon dioxide and calcium carbonate:



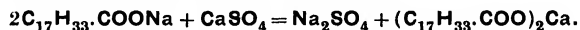
Carbon dioxide cannot remain dissolved in boiling water, all dissolved gases being expelled at  $100^{\circ}\text{C}$ . Removal of the carbon dioxide causes the carbonates to become again insoluble, and if, after the water has been boiled, it is allowed to stand, the calcium and magnesium carbonates will settle down as a precipitate, and the clear water will contain no hardness, *i.e.* it will be *soft*. Hardness which is due to the presence of bicarbonates and which can be removed by boiling is said to be *temporary*.

**Permanent Hardness.**—The sulphates and chlorides of calcium and magnesium are soluble in water, in both the presence and the absence of carbon dioxide. Expulsion of the dissolved carbon dioxide makes no difference to their solubility. They are not, therefore, precipitated when the water is boiled, but remain in solution. Hardness due to these salts, which is not removed by boiling, is called *permanent hardness*.

**Methods of expressing Hardness.**—In stating the hardness of a water it is usual to express it in terms of calcium carbonate, and this applies to both temporary and permanent hardness, irrespective of whether they are due to salts of calcium or of magnesium. Hardness is described quantitatively in two ways, *viz.* (1) degrees, and (2) parts per 100,000. Degrees of hardness are grains per gallon. Thus  $10^{\circ}$  means that one gallon of water contains 10 grains of hardness expressed as calcium carbonate. If the hardness of a water is 10 per 100,000, it means that 100,000 parts of water contain 10 parts by weight of hardness, again expressed as calcium carbonate. A gallon of water contains 70,000 grains, and one pound 7000. Hence parts per 100,000 may be converted into grains per gallon by multiplying by 0.7, and vice-versa grains per gallon divided by 0.7 give parts per 100,000.

Thus 5 grains per gallon =  $\frac{5}{0.7}$ , or 7.1 parts per 100,000.

**Properties of Hard Water.**—If distilled, or soft, water be shaken with a solution of soap, the latter dissolves and forms a lather or foam, and only a very small amount of soap is required. But if a dilute solution of soap be added drop by drop to some hard water in a stoppered bottle, which is closed and shaken after each addition, the result will not be the same. At first the water becomes turbid and no lather is produced when the bottle is shaken. Further, gradual addition of the soap solution changes the turbidity into a white precipitate, which consists of insoluble calcium or magnesium soap. With a soap made from oleic acid the reaction is



When the whole of the calcium and magnesium compounds present in the water have been changed into insoluble soaps, further addition of soap solution will give a lather. Naturally, the quantity of soap necessary to give a permanent lather depends upon the calcium and magnesium salts present—that is, on the hardness of the water. For each gallon of soft or pure water about 10 grains of soap are required, while for each degree of hardness about 6 grains more are necessary. The first objection to the use of hard water is, then, that it causes a great waste of soap. But of even more importance is the fact that if these insoluble calcium and magnesium soaps are deposited on the fabrics, they render them impermeable in subsequent processes. In dyeing, for example, this would prevent the dye liquor from penetrating them, and the colour would be unevenly distributed. Calcium and magnesium soaps when freshly prepared are white in colour. But if they are dried they become gradually yellowish or brown, thus spoiling the colour of white goods which contain them. If the original soap was made from an oil with a

characteristic odour, such as cotton-seed oil, this is developed by the gradual decomposition of these insoluble soaps. Hard waters are also undesirable in many dyeing operations. If used in boilers they cause scale. They may also have a corrosive action on the boiler plates and cause foaming or priming.

**Scale-forming Waters.**—All hard waters produce scale. The composition of this and its hardness depend upon the rate of evaporation and the constituents of the water. It may vary in appearance from a granular deposit which is easily removed, to a hard solid mass which adheres firmly to the boiler plates and requires chipping off with a hammer and chisel. A scale of this kind not only wastes heat, owing to its being a bad conductor, but causes unequal heating of the plates, which gradually wears them out.

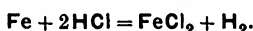
**Corrosive Waters.**—Corrosion of boiler plates is one of the chief difficulties attending the use of natural waters. The chief causes of boiler corrosion are

- (1) The presence of salts, like magnesium chloride, which dissociate on heating.
- (2) Neutral sodium salts.
- (3) Bicarbonates.
- (4) Dissolved oxygen and carbon dioxide.
- (5) Variations in composition of the boiler plates.

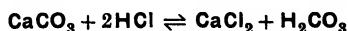
(1) *Dissociable Salts.*—Magnesium chloride dissociates when heated in the presence of steam, giving magnesium oxychloride and hydrochloric acid:



The hydrochloric acid liberated dissolves the iron of the boiler plates, forming ferrous chloride, or distils over with the steam:



Bailey (*J. Soc. Chem. Ind.*, 1899, **18**, 456) states that the liberated hydrochloric acid may accumulate in the boiler, and that damage may be done to the boiler plates long before any acid can be detected in the steam. The decomposition of magnesium chloride is more rapid if the iron is in contact with another metal such as copper or brass, since in this case an electric couple is formed which assists the reaction. This corrosion is more apparent at such places. Slight local differences in the composition of adjacent boiler plates are sufficient to induce electrochemical action. Magnesium chloride is quite common in hard waters, and may sometimes be present in softened water. Its dissociation is inhibited by the presence of a little caustic alkali. Corrosion caused by magnesium chloride is essentially acid corrosion. In connection with this acid corrosion, Heinzelmann (*J. Soc. Chem. Ind.*, 1914, **33**, 1079) made the interesting observation that at high pressures silicic acid, if present in water, could liberate stronger acids, such as hydrochloric, sulphuric, and nitric, from their sodium salts. R. L. Taylor has shown that the reaction:



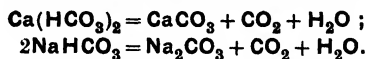
is reversible. Thus, under certain conditions, carbonic acid can liberate hydrochloric acid from chlorides. Both unsoftened and softened water are liable to contain either carbon dioxide or bicarbonates, and this is another possible cause of acid corrosion.

(2) *Neutral Salts.*—Many natural and all softened waters contain such salts as sodium sulphate, chloride, and nitrate. Solutions of these attack iron at the temperature of the boiler. The rate of dissolution of the iron increases

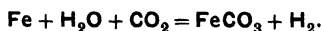


with the concentration up to a certain point, and is assisted also by the presence of another metal which could form an electric couple. Dissolved oxygen greatly accelerates the action of neutral salts, and it is thought by many chemists that in the complete absence of oxygen they have no deleterious action.

(3) *Bicarbonates*.—These when heated give rise to carbon dioxide, thus:

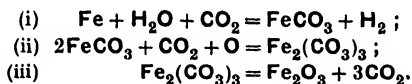


Carbon dioxide attacks iron, forming ferrous carbonate,  $\text{FeCO}_3$ :

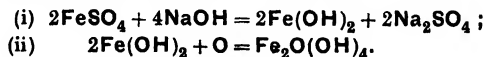


Hard water always contains calcium or magnesium bicarbonate, while sodium bicarbonate is commonly present in softened water.

(4) *Dissolved Oxygen and Carbon Dioxide*.—Dissolved oxygen is the chief cause of corrosion, especially if carbon dioxide is also present. We have seen that carbon dioxide converts iron into ferrous carbonate. But this action ceases as soon as all the carbon dioxide has entered into combination. If any oxygen is present, however, it is quite different. The ferrous carbonate is then oxidized to ferric carbonate. This is decomposed, at the temperature of the boiler, into ferric oxide and carbon dioxide. The latter then forms ferrous carbonate, thus starting the cycle again, which may continue indefinitely:



All natural waters contain dissolved oxygen. Surface and subsoil waters are often fully saturated. Those from deep wells contain less, but generally at least 0.2 part per 100,000. No water-softening process removes oxygen; in fact, owing to agitation or mixing, the oxygen is liable to be increased by softening. While making the water more suitable for bleaching and dyeing, we may, therefore, at the same time make it more corrosive by (1) increasing the amount of dissolved oxygen, (2) leaving bicarbonates in it, and (3) adding sodium salts. Modern practice in treating feed waters is largely directed to removing dissolved oxygen and carbon dioxide; but carbon dioxide is comparatively harmless in the absence of oxygen. The simplest way of removing oxygen is to heat the feed water to the boiling-point before it enters the boiler. This expels all the dissolved gases. Oxygen may also be removed by a chemical process, by treating the water with the quantities of ferrous sulphate and sodium hydroxide required by the equations:



Other processes are also used, including the following:

(a) The hot feed water is brought into contact with thin sheets of iron in a "deactivating tank," where the corrosive action is exerted on a cheap metal instead of on expensive boiler plates.

(b) The water is sprayed over baffles in a deactivator, and the gases are removed by heat or vacuum, or a combination of both.

(c) A counter electromotive force higher than that causing corrosion is introduced into the boiler. For example, in the Cumberland process the shell of the boiler forms the cathode, the anode consisting of pieces of iron

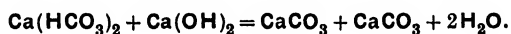
inserted in the water and insulated from the shell. A continuous current (D.C.) is supplied by a dynamo.

(5) *Variation in the Composition of Boiler Plates.*—According to C. H. Desch (*J. Soc. Chem. Ind.*, 1917, **36**, 855) local couples are caused chiefly by want of homogeneity in the boiler plates. This may be due to either chemical or physical differences. Chemically pure metals may corrode by reason of local physical differences induced by mechanical means, such as cold working, by which films of amorphous iron are formed between the separate crystal grains.

**Foaming Waters.**—Waters containing organic or suspended matter often foam naturally, but a more common cause is the presence of excess of alkali or of salts of sodium. It was found by M'Gill (*J. Soc. Chem. Ind.*, 1904, **23**, 351) that all sodium salts produce foaming at 100° C. if present to a greater extent than one gram per litre. When water is heated under pressure the quantity necessary to cause foaming becomes less. Water containing 300 parts per million of any sodium salt reckoned as sodium oxide ( $\text{Na}_2\text{O}$ ) is unsuitable for steam-raising purposes.

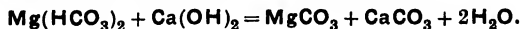
**Water-softening.**—If water contains more than 5 parts of hardness per 100,000 it is likely to cause trouble in bleaching or dyeing. The hardness can be removed by a process termed *softening*.

**Removal of Temporary Hardness.**—It has been stated above that temporary hardness can be removed by boiling the water and thus expelling the carbon dioxide. This method is suitable for small lots of water such as might be used in making up a dye-bath, but would be impracticable for large quantities. But the carbon dioxide can be removed, also, by adding a base which combines with it. Lime or calcium hydroxide is generally used for this purpose. If clear lime-water is added to water containing temporary hardness, a white precipitate will be formed. This consists of calcium carbonate, formed by the union of the lime with the carbon dioxide of the calcium or magnesium bicarbonate:

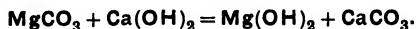


Whilst calcium bicarbonate is soluble in water, the normal carbonate is not. Thus the addition of lime causes the precipitation of the whole of the temporary hardness caused by calcium bicarbonate. The equation shows that for 100 parts of temporary hardness 56 parts of quicklime are required.

The removal of magnesium bicarbonate is not quite so simple. When calcium hydroxide is added to water containing magnesium bicarbonate, calcium and magnesium carbonates are formed:



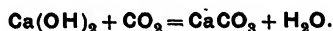
But the magnesium carbonate is not precipitated till a second molecule of lime or calcium hydroxide has been added, which converts it into insoluble magnesium hydroxide:



Thus, each molecule of magnesium bicarbonate present requires two of lime for complete precipitation. That is, every 100 parts of temporary hardness, expressed as calcium carbonate, due to magnesium require  $2 \times 56 = 112$  of quicklime for precipitation. Sodium hydroxide can be used instead of lime, soluble sodium carbonate being formed:

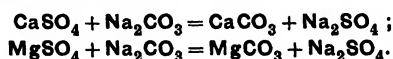


Water often contains free or dissolved carbon dioxide, which will combine with some of the lime :

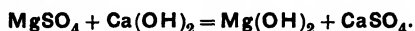


Hence, in order to calculate the exact quantity required to remove temporary hardness the free carbon dioxide must also be known and allowed for.

**Removal of Permanent Hardness.**—Both calcium and magnesium sulphates, and other soluble salts, are decomposed by sodium carbonate, with the formation of carbonates and sodium sulphate, etc. :



The calcium sulphate is thus removed as calcium carbonate, an equivalent quantity of sodium sulphate being left in solution. Magnesium sulphate would be converted into magnesium carbonate, and this would require to be precipitated by means of lime. But if enough lime is added to precipitate all the magnesium present, the magnesium sulphate is converted into calcium sulphate, and the total amount of permanent hardness is not altered, thus :



The calcium sulphate is then decomposed by sodium carbonate.

**Quantities of Lime and Sodium Carbonate required.**—It is obvious that in order to calculate the quantities of lime and sodium carbonate necessary for softening any given volume of hard water, we must know—

- (1) The temporary hardness.
- (2) The hardness due to magnesium, whether temporary or permanent.
- (3) The permanent hardness.
- (4) The free carbon dioxide.

The calculation is made in the following manner :

One part of hardness per 100,000 of water—

Caused by	Quicklime required.	Sodium Carbonate required.
Calcium bicarbonate . . .	0.56	..
Magnesium bicarbonate . . .	2 × 0.56	..
Magnesium sulphate . . .	0.56	..
Calcium sulphate . . .	..	1.06

The hardness due to magnesium forms part of the temporary hardness as well as of the total hardness due to magnesium salts. The sum of the temporary and total magnesium hardness will include the temporary magnesium hardness twice over. Thus, the quicklime required will be the sum of these two multiplied by 0.56. The following is an example :—

Temporary hardness . . . . .	10 per 100,000
Magnesium hardness . . . . .	5 per 100,000

Then  $(10 + 5) \times 0.56 = 8.4$  parts of quicklime per 100,000 of water are required. Every 44 parts of free carbon dioxide require in addition 56 parts of lime.

The quantity of sodium carbonate required is 1.06 for each part of permanent hardness per 100,000 of water.

These figures would be correct only for pure chemicals. If the lime contained 95 per cent. of  $\text{CaO}$ , and the sodium carbonate 98 per cent. of the

anhydrous salt, the quantities would have to be multiplied by 100 and divided by 95 and 98 respectively.

The figures given above may be reduced to convenient formulæ:

Let  $H_t$  represent temporary hardness,  
 $H_p$  „ permanent hardness,  
 and  $H_m$  „ hardness due to magnesia;

then

Quicklime in lb. required per 100,000 gall. =  $5.6 (H_t + H_m)$ ;

Dry sodium carbonate in lb. required per 100,000 gall. =  $10.6 \times H_p$ .

To remove temporary hardness alone by means of lime the quantity required is

$.56 (H_t + H_m - H_p)$  where  $H_m$  is greater than  $H_p$ ;  
 $.56 (H_t + H_m)$  where  $H_m$  is not greater than  $H_p$ .

(Parts per 100,000 are the same as pounds per 10,000 gallons.)

As a rule, the calculated quantities require some adjustment. A Winchester bottle full of water should be treated first. After the precipitate has settled

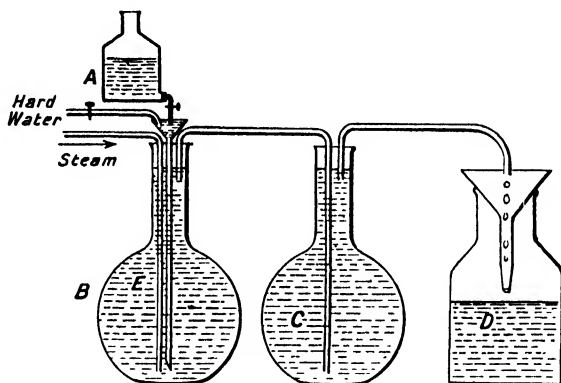


Fig. 26.—Water-softening Experiment.

the clear water is tested by the methods given later, and the quantities of chemicals are adjusted if necessary.

**Water-softeners.**—Water-softening is carried out on the industrial scale by means of automatic apparatus. These are of two kinds, namely, *intermittent* and *continuous*. In the former the water is mixed with the necessary chemicals, the precipitated hardness allowed to settle, and the clear softened water then drawn off. In the continuous form the precipitate is removed partly by gravity, but chiefly by means of a filter. This form of apparatus is more convenient since it requires much less room. The essential parts of a water-softener are (1) a reagent tank, (2) a reaction tank, (3) a precipitating tank connected generally with a filter, (4) a soft-water tank.

The principles of their action are illustrated by the apparatus shown in Fig. 26. *A* is a small cistern containing a mixture of sodium hydroxide and carbonate. This flows through a funnel into the corked reaction chamber *B*, entering at the bottom, and at the same time becoming mixed with the hard water entering from the main supply. The concentration of the chemicals and the rate of flow are such that in a given time approximately sufficient of the reagents are delivered to soften the water entering the reaction chamber

during the same time. Through a second tube *E*, also reaching to the bottom of the flask, steam is passed to assist complete mixing and chemical reaction. A third tube, commencing just beneath the cork, leaves the flask *B* and passes to the bottom of a second corked flask *C*, which is the precipitating chamber.

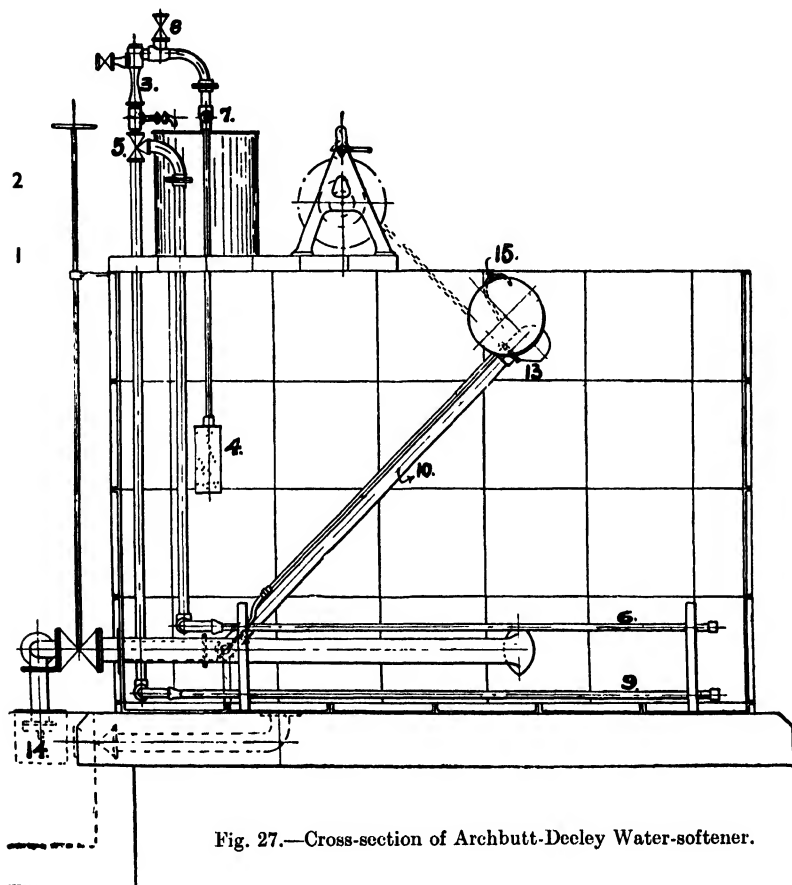


Fig. 27.—Cross-section of Archbutt-Deeley Water-softener.

A second delivery tube leaves this chamber at the top, ending above a filter leading to the store tank *D*.

*Archbutt-Deeley Water-softener*.—This is one of the best known of the intermittent forms. It can be used with advantage when a continuous supply of softened water is not required. For 6000 gallons per hour one softening tank is sufficient, but for a greater volume two or more are required. The apparatus is shown in Fig. 27. The water to be softened is run into the tank by means of the pipe (1) up to a gauge mark on the side. At the same time the calculated quantities of lime and sodium carbonate are weighed into the small tank (2), mixed with water, and boiled with live steam. When the tank is full of water up to the gauge mark the inlet valve is closed and steam is passed through the blower (3). This causes a current of water to circulate through the rose (4) and the three-way tap (5), and then into the tank through perforations in a row of horizontal pipes (6). The three-way tap is then opened

and the solution or mixture of the chemicals run into the tank by means of the currents caused by the steam. Air is then blown through the pipe (6) by opening the taps (7 and 8), and then by reversing the tap (5) through the perforators in the underside of the tube (9) to stir up the old precipitate which was left in the tank. After air has been blown in for about ten minutes, the precipitate is allowed to settle for an hour. The clear softened water is drawn off through the floating mouth (13 and 15) of the hinged pipe (10). As the water flows down this pipe it meets an ascending stream of carbon dioxide produced by burning

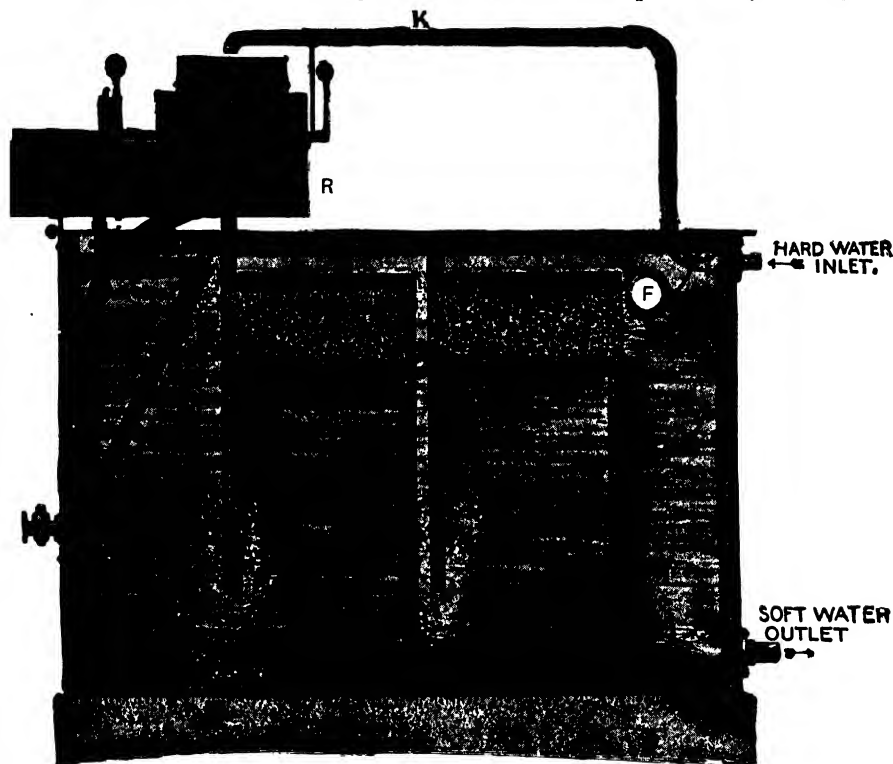


Fig. 28.—Lassen and Hjort Water-softener.

coke. This converts any traces of lime or magnesium into soluble bicarbonates, thus preventing them from clogging the feed pipes. The softened water is run to a store tank. The precipitate or sludge is removed from time to time from the bottom of the tank (14).

*Lassen and Hjort Water-softener.*—This is a very good type of continuous as distinguished from non-continuous water-softener, such as the Archbutt-Deeley type. There are three essential features: the reaction chamber, the settling chamber, and the filter. In an intermittent water-softener the filter is dispensed with, the precipitate being merely allowed to settle before the soft water is drawn off. In this process, however, a constant stream of hard water is led into a reaction chamber, where it comes into contact with the chemicals, the mixture being heated by live or waste steam in order to make the softening more complete, it being possible to soften a water more completely when the temperature is raised than when heating is dispensed

with. From the reaction chamber the water passes into the settling chamber, and thence up through a suitable filter, and finally into a storage tank. The lime in this process is used in the form of milk of lime, which is about 100 times as strong as lime-water, thus making it possible to reduce the size of the chemical tank. It is claimed by the proprietors of this patent that the strength of the lime solution is always known.

The hard water passes along the pipe *K* (Fig. 28) into one of the chambers of the oscillating receiver *R*. When this chamber fills, the centre of gravity is altered, causing it to tip up and pour its contents into the tank *B*, at the same time bringing the other chamber of the receiver under the orifice of the

pipe *K*. To the side of the oscillating receiver is fitted a tank *D* containing the chemicals—lime and soda-ash, or caustic soda. A valve is fitted to the bottom of *D*, actuated by a system of levers fitted to the oscillating receiver, so that at each oscillation a given quantity of the chemicals can be mixed with the water. The water in the chamber *B* is heated to about 150° F. (65° C.) by means of live or exhaust steam. From *B* the water passes through settling tanks *A*, and from these upwards through filters of wood-wool packed tightly between rows of wooden bars. After softening and filtering, the water flows into a storage tank *O*. The storage tank is fitted with a pressure float *F*, which regulates the flow of water in the pipe *K* according to the height of water in the tank *O*.

#### *Paterson Vertical Softener.*—

A vertical apparatus is often preferable to the horizontal form.

An illustration of a Paterson vertical softener is shown in Fig. 29. The water and chemicals enter the apparatus at the upper end of the inverted funnel *A*, fall to the bottom, and then rise upwards through the filter *B* at the top, the softened water issuing at *C*.

In order to get good results with any kind of automatic water-softener, it is important that the apparatus should not be worked beyond its capacity. The precipitation is not instantaneous, but gradual, and if the mixture of hard water and chemicals passes through the apparatus too quickly it will go through the filter before precipitation is complete. The chemicals used must have a known composition and be checked by analysis. A formula calculated on the assumption that the lime used is of 95 per cent. purity cannot give good results if the sample contains only 75 per cent. of true lime. Calcium carbonate is not absolutely insoluble in water, and no process which relies upon the

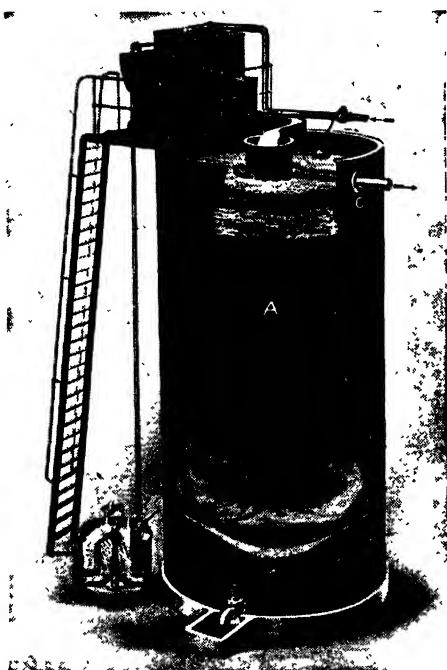
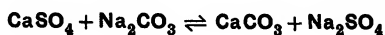


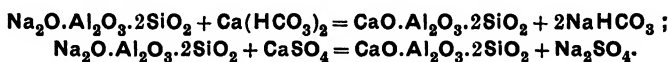
Fig. 29.—Paterson Vertical Cylindrical Type Water-softener.

precipitation of this body can give, therefore, a water with what is termed "zero" hardness. A residual hardness of from two to three parts per 100,000 is the best that can be expected. In all of these processes it should be noted that while, when temporary hardness is removed, nothing is left in solution beyond that due to the solubility of calcium carbonate, yet permanent hardness cannot be removed without leaving an equivalent quantity of sodium sulphate. When very hard waters have to be softened this becomes a matter of some importance. A difficulty inseparable from the lime-soda process is that the equation:

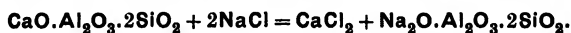


is reversible, the degree of reversibility depending upon the concentration of the sodium sulphate. This prevents complete softening in the case of waters containing much permanent hardness. Magnesium hydroxide tends to form a colloidal solution, which passes through the filter. This can be prevented, however, by adding 2 to 3 parts of sodium aluminate per 100,000 parts of water.

**Permutit Process of Water-softening.**—This method, which is to a large extent replacing the use of lime and sodium-carbonate softeners, depends upon the use of zeolites. These are hydrated silicates of aluminium containing calcium or sodium. They occur naturally or may be manufactured artificially. Artificial zeolites containing sodium are termed *permutits*. They have the composition represented by the formula  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ . Permutits are quite insoluble in water. When sodium permutit is brought into contact with an aqueous solution of a salt of calcium or magnesium, the sodium is exchanged for the alkaline-earth metal, the sodium salt of the acid remaining in solution, and calcium or magnesium permutit being formed. If an excess of sodium permutit is present the whole of the calcium or magnesium is removed. With calcium bicarbonate and sulphate the reactions are



It should be noted that when temporary hardness is removed an equivalent quantity of sodium bicarbonate is left in solution. For certain purposes, such as dyeing with basic dyestuffs, this has to be taken into account. In order to soften water by means of permutit the substance is ground into small pieces or granules, and the hard water is allowed to percolate slowly through a layer of these granules. Since, in this case, we have no complication due to the solubility of calcium carbonate, the water which issues from the permutit filter is quite free from both calcium and magnesium, *i.e.* its hardness is "zero." The reaction continues until all the sodium permutit is changed into the calcium or magnesium salt. This is indicated by the water issuing from the filter becoming hard. If the calcium or magnesium permutit is now treated with a solution of common salt, the sodium permutit is regenerated:



The soluble calcium chloride is carried away with the salt solution. The residual salt and calcium chloride are washed away with soft water, and the regenerated sodium compound can now be used again. The process can be continued indefinitely, subject only to wear and tear of the permutit.

An illustration of the apparatus used is given in Fig. 30.

Since each molecule of calcium or magnesium bicarbonate present in the



original water gives rise to an equivalent of sodium bicarbonate, the alkalinity of the softened water will always be equivalent to the temporary hardness. Though an absolutely soft water can be produced, the quantity of permutit

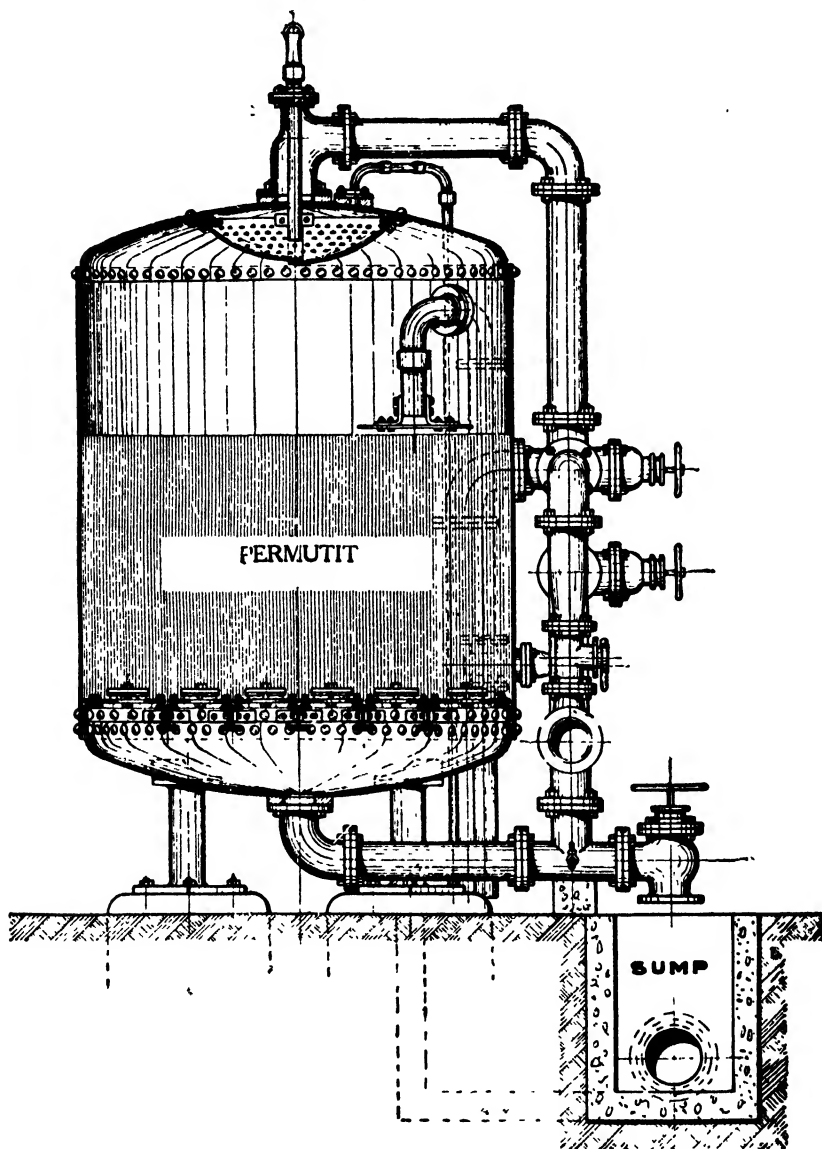
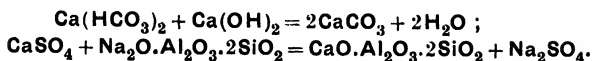


Fig. 30.—Permutit Softener.

required per 1000 gallons and that of salt for its regeneration are considerable in the case of really hard waters. For these reasons, it is often more economical to combine the permutit with a precipitation process. For example, the temporary hardness may first be removed by means of lime, leaving only the

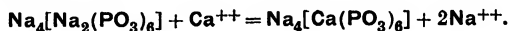
permanent hardness to be dealt with by the permutit :



The base-exchanging methods such as the permutit process have certain disadvantages: (1) The alkalinity of the softened water makes it unsuitable for certain textile processes, and causes priming and corrosion in boilers. (2) The permutit is dissolved gradually by water containing carbon dioxide, and suffers loss also by attrition. (3) It is attacked by dilute acids, and is affected by iron. (4) If oil be present in the water, it forms a protective film on the material, and suspended matter in the water gradually chokes the filter. (5) In the case of water containing much hardness the cost is prohibitive owing to the quantity of salt required.

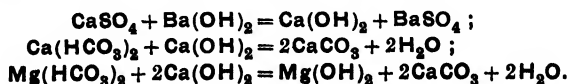
**Choice of Method used.**—This will depend upon the nature and quantity of the hardness, and the alkalinity of the water if softened by a base-exchanging process. When the total hardness does not exceed 5 parts per 100,000, the water can be used unsoftened for nearly every textile process. If the total hardness does not exceed 15 parts per 100,000 a base-exchanging process is suitable. When the temporary hardness is high but the permanent hardness comparatively low, the lime-soda method is applicable. If, for example, the temporary hardness were 15 per 100,000 and the permanent hardness 5 per 100,000, the lime-soda process would give good results. If the temporary and permanent hardness were 25 and 5 per 100,000 respectively, the cost of softening by means of permutit would be high, and the softened water would contain 42 parts of sodium bicarbonate per 100,000. This could be avoided by removing the temporary hardness with lime before passing the water through a permutit plant. In the case of both temporary and permanent hardness being high, *e.g.* 25 and 10 respectively, the water might be softened first with lime and sodium carbonate, and then treated with permutit.

**Use of Sodium Hexametaphosphate.**—The chief objection to the use of hard water in textile processes is that it causes the deposition of insoluble calcium soaps in the goods. This can be prevented in the case of water containing only a moderate amount of hardness by adding sodium hexametaphosphate to the scouring bath. This reacts with calcium ions in accordance with the equation :



The calcium compound formed does not precipitate calcium soaps, nor reduce the efficiency of the scouring liquor. Sodium hexametaphosphate is sold under the name of "Calgon." Not only does it prevent the deposition of calcium soaps, but also it removes them from fabrics which contain them. The alkalinity of the bath should be about pH 8.3.

**Use of Barium Salts.**—When only permanent hardness has to be considered, it may be removed completely by barium chloride. This method of treatment is applicable to feed water for boilers, in which calcium sulphate produces a troublesome scale, whilst barium sulphate is granular and does not form scale. Moreover, barium chloride is not hydrolysed in the boiler, and hence does not cause corrosion if a small excess is left. Barium hydroxide will precipitate both temporary and permanent hardness in accordance with the equations :



Regularity in twist also is largely dependent on uniformity of diameter. When fine and coarse fibres are twisted together about a common longitudinal axis the number of twists per inch is greater where the fibres are fine than it is where they are coarse.

Fibres which are deficient in tensile strength are sometimes strengthened artificially by *sizing* during the manufacturing process. Sizing consists in treating with a solution of a colloidal adhesive substance, such as starch or glue, which can be washed out of the finished fabric.

Fabrics are either woven or knitted. Woven fabrics contain two kinds of threads, termed *warp* and *weft*. The warp threads run throughout the length of the fabric, forming the skeleton and taking the strain of manufacture and wear. These must possess a high degree of elasticity and tensile strength. The weft threads run transversely, filling up the spaces between the warp threads. They give body to the fabric, but are not exposed to such strain in manufacture and wear as the warp threads. Yarns designed for wefts require filling power rather than strength. Fibres and yarns which have insufficient strength for warp are still suitable for weft threads. A knitted fabric is made from one thread or double thread, and there is no differentiation into warp and weft.

### Classification of Textile Fibres.

All the textile fibres of commerce belong to one of the following classes:—

- (1) Unicellular vegetable hairs—cotton.
- (2) Multicellular vegetable fibres—flax, ramie, hemp, jute.
- (3) Animal secretions—silk.
- (4) Appendages of the epidermis of animals—wool, hair.
- (5) Artificial fibres obtained by modification or regeneration of cellulose, generally termed *rayon*—viscose rayon, nitro rayon, cuprammonium rayon, acetyl (cellulose-acetate) rayon.
- (6) Artificial fibres produced by polymerisation of relatively simple monomers—nylon, vinyon.
- (7) Artificial fibres produced from proteins—lanital.
- (8) Mineral fibres—asbestos, glass.

Cotton consists of unicellular hairs produced by the seed to assist its distribution; multicellular fibres are bast fibres obtained from the stems of plants. Silk is a solidified viscous liquid secreted by the silk-worm to form the cocoon. Wool and hair are outgrowths of the epidermis of animals, and are composed of cells similar to those of the epidermis. Artificial fibres may be either of vegetable or of animal origin, or they may be polymers of relatively simple organic compounds. The older-established rayons are made from cotton, cotton linters or paper pulp. Recent additions to the range of man-made fibres are Nylon, which is made from hexamethylene-diamine and adipic acid, and Vinyon, derived from vinyl chloride and vinyl acetate. Protein fibres are made from casein derived from milk or proteins of vegetable origin, such as soya bean or the ground-nut. Lanital consists of casein obtained from milk.

The nature of a fibre may generally be determined by microscopic examination, as will be seen later, but there are certain simple chemical tests which may be applied.

**Vegetable fibres** burn readily with a clear flame and without producing any smell. When heated in a dry test-tube they give acid vapours. They dissolve in cold concentrated sulphuric acid, but are insoluble in boiling 5 per cent. sodium hydroxide solution.

**Animal fibres** do not burn freely, but frizzle, giving the characteristic odour of burning wool. When heated in a dry test-tube they give off ammonia, and in the case of wool sulphuretted hydrogen also. They are readily soluble in a boiling 5 per cent. solution of sodium hydroxide, and the solution obtained with wool contains sulphides. All animal fibres are dyed when boiled with a decolorized solution of magenta (Schiff's reagent).

**Mineral fibres** are incombustible and insoluble in acid or alkali.

### Special Tests for the Different Fibres.

**Cotton.**—Cotton is insoluble in a boiling 5 per cent. solution of sodium hydroxide. It dissolves rapidly in cold concentrated sulphuric acid, and if the solution be poured into excess of cold water, a precipitate of cellulose hydrate is formed. If, however, the solution be allowed to stand for some time, no precipitate is formed, but the solution gives reactions for glucose. When treated with a solution of iodine in potassium iodide and dilute sulphuric acid, cotton is stained blue, and the same result is obtained with zinc chloriodide solution. Zinc chloriodide solution is made by dissolving 1 g. of potassium iodide in a solution of 5 g. of potassium iodide in 16 ml. of water and adding a solution of 25 g. of zinc chloride in 16 ml. of water. Cotton dissolves slowly in a concentrated solution of zinc chloride and in cuprammonium solution, from which solutions it can be precipitated by dilution or, in the case of cuprammonium, by neutralization with acid.

Raw and bleached cotton may be distinguished by the fact that the former has a distinct affinity for acid and basic dyestuffs owing to the presence of proteins. 0.1 g. of the sample is immersed for 30 to 60 seconds in 10 ml. of a boiling solution of Victoria Blue B containing 3 per cent. of the dyestuff on the weight of the sample, i.e. 0.003 g., then washed in cold water, immersed for 1 minute in boiling water, again washed with cold water, and finally dried. Raw cotton fibres will be coloured uniformly; bleached fibres will be only slightly stained.

**Multicellular Vegetable Fibres.**—These give the same general reactions as cotton, but are identified readily by microscopic examination. When the separate fibres are examined microscopically, those of flax are seen to taper to a point, whilst those of hemp have a rounded or knotty end. Flax and hemp may be distinguished also by the following test: Fibres teased out from the sample are soaked in warm water and allowed to dry in air or over a warm plate. The fibres of flax and ramie always twist in a clockwise direction, whilst in the case of hemp and jute the twist is anti-clockwise. Jute contains a considerable quantity of lignocellulose, which is identified by the fact that it is stained yellow by a solution of aniline sulphate, and red by phloroglucinol. For the latter test the sample is soaked in a 10 per cent. alcoholic solution of phloroglucinol containing a little hydrochloric acid, and then heated on a water-bath. Hemp gives also a faint reaction.

**Silk.**—This is identified by the following tests: It dissolves in cold concentrated hydrochloric acid or a boiling 5 per cent. solution of sodium hydroxide. If lead acetate be added to the latter solution, no precipitate of lead sulphide is obtained. Silk dissolves also in Loewe's and Richardson's solutions. These are made in the following manner:

**Loewe's Solution.**—To 100 ml. of a 10 per cent. aqueous solution of copper sulphate add 5 ml. of glycerol and then 50 per cent. sodium hydroxide solution until the precipitate of copper hydroxide is just dissolved.

**Richardson's Solution.**—Twenty-five grams of nickel sulphate is dissolved in water and treated with a slight excess of sodium hydroxide. The precipitated nickel hydroxide is filtered off, washed with water, dissolved in 125 ml. of strong ammonia solution, and diluted to 250 ml. with water.

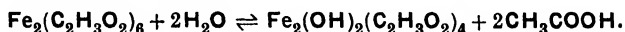
Silk is stained yellow by a solution of picric acid, and is dyed when boiled with Schiff's reagent.

**Wool and Hair.**—These fibres give the following reactions: (1) They are insoluble in cold concentrated hydrochloric acid. (2) When they are dissolved in a boiling 5 per cent. solution of sodium hydroxide, the solution obtained gives a positive reaction for sulphides with lead acetate solution or sodium nitroprusside. (3) They are stained yellow with picric acid solution, and dyed with boiling Schiff's reagent.

**Casein fibres**, such as lanital, usually give off formaldehyde when distilled with dilute sulphuric acid. They dissolve in boiling sodium hydroxide solution, but the solution does not contain sulphides. Wool and casein fibres may be distinguished by the following tests (Whittaker, *J. Soc. Dyers Col.*, 1937, 53, 468):

If wool and casein fibres are immersed for one minute in a cold solution of 0.5 g. of certain wool dyes and 0.5 ml. of 80 per cent. sulphuric acid per 100 ml. of water and then rinsed, the casein fibre will be dyed a full shade, whilst wool will be only slightly stained. Xylene Light Yellow 2G, Azogeranine 2GS, and Erio Fast Cyanine S are suitable dyes. With Neocarmine W, casein is stained a deep orange, wool bright yellow. Wool shows a weak violet fluorescence in ultra-violet light, casein fibre a dead white.

**Artificial Vegetable Fibres.**—*Cellulose acetate (acetyl rayon)* is soluble in warm acetone and insoluble in cuprammonium solution. When heated with sodium hydroxide solution it is converted into cellulose and sodium acetate. If the mixture be filtered, and the filtrate concentrated and acidified with sulphuric acid, the smell of acetic acid can be observed. Alternatively, the filtrate may be exactly neutralized with sodium hydroxide solution, and a little neutral ferric chloride solution added. A red colour will be produced, and on boiling the mixture a red precipitate of basic ferric acetate is formed in accordance with the equation:



*Nitro, cuprammonium, and viscose rayons* all consist of regenerated cellulose, but contain traces of impurities, which assist in their identification. Nitro rayon contains residual nitro groups, which can be detected in the following manner: if a little of the sample is treated with a solution of diphenylamine in concentrated sulphuric acid a deep blue colour is produced. Viscose may contain free sulphur, and cuprammonium traces of copper. Viscose gives a brown colour with Rhode's solution; other rayons do not. Rhode's solution is made as follows: 1 g. of silver nitrate is dissolved in 10 ml. of water and added to a solution of 4 g. of sodium thiosulphate in 100 ml. of water. After allowing the precipitate which is formed at first to dissolve, a solution of 4 g. of sodium hydroxide in 100 ml. of water is added, and the mixture boiled and filtered. The rayon is immersed in the reagent for one minute at the boiling-point. Copper can be tested for in the ash of cuprammonium rayon. Ruthenium red,  $\text{Ru}_2(\text{OH})_2\text{Cl}_4(\text{NH}_3)_7 \cdot 3\text{H}_2\text{O}$  (0.1 g. in 10 ml. of water), gives the following colours: viscose, pink; nitro rayon, violet; cuprammonium rayon, faint pink. Wagner's reagent (picrocarmine K) stains cuprammonium dark red but viscose remains uncoloured.

## CHAPTER VIII.

### PHYSICAL AND CHEMICAL TESTS FOR TEXTILE FIBRES.

#### Moisture Content of Textile Fibres and Capacity for Absorbing Water.

ALL textile fibres have a certain power of attraction for atmospheric moisture. This affinity is due to physical causes rather than that the moisture taken up enters into chemical combination. The absorption of moisture by fibres from the atmosphere is therefore a reversible process. In damp air they may take up moisture from the atmosphere, whilst in dry air they may give it off. As with all reversible phenomena, the moisture content of a textile material under any given set of circumstances represents a state of equilibrium between the following factors:

- (1) Attraction of the fibre for water under existing conditions of temperature, etc.
- (2) Readiness of the air to give up moisture under the same conditions, i.e. whether the air itself is in a damp or a dry state.

**Relative Humidity of Atmosphere.**—Since the state of the air is one of the factors controlling the moisture content of textiles, it would be advisable to discuss this briefly before considering in detail the properties of the fibres themselves. The *relative humidity* of the atmosphere is the term used to describe the dampness of the air. The quantity of water which air can take up is limited by the condition that the pressure of its vapour, independently of that of the air, cannot exceed a certain value for any given temperature. The maximum pressure is the same as that which the water vapour would exert if no air were present. The actual pressure of air saturated with water vapour is the sum of the two pressures, i.e. the pressure of the atmosphere and the maximum pressure of water vapour at the atmospheric temperature.

The dampness or the dryness of air depends upon the pressure of the water vapour present, compared with its maximum for the atmospheric temperature. The nearer the actual pressure of the water vapour present approaches to the maximum, the damper the air is, and, on the other hand, the farther apart these two pressures are the drier it is. When the water exerts the maximum vapour pressure for the atmospheric temperature, and no more can be taken up, the air is said to be *saturated*. When damp textile materials are exposed to saturated air they cannot lose any moisture, but if they are in a dry state they can take water from the air.

*Relative humidity* is the term used to express the actual state of the air with regard to its moisture content. This term is really the percentage which the actual vapour pressure of the moisture present is of the maximum vapour pressure corresponding with the atmospheric temperature. Expressed in another way:

$$\text{Relative humidity} = \frac{p}{p_1} \times 100,$$

where  $p$  represents the actual pressure of the water vapour, and  $p_1$  the maximum pressure at the same temperature.

**Determination of Relative Humidity.**—The relative humidity of the air is commonly determined with the wet- and dry-bulb thermometer. This consists of two thermometers mounted side by side. The bulb of one is directly exposed to the air. The bulb of the other is covered by a wick or a piece of flannel, the other end of which is immersed in a container of water. Such a thermometer is illustrated in Fig. 31.

As water evaporates from the wick surrounding the bulb of the wet thermometer, the temperature of the surrounding air will be lowered. The

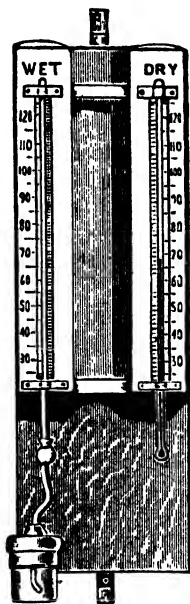


Fig. 31.—Wet- and Dry-bulb Thermometer.

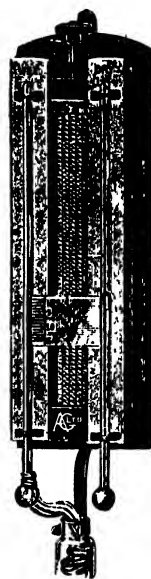


Fig. 32.—Roller-type Hygrometer.

decrease of temperature will be directly proportional to the rate at which evaporation takes place, which, in its turn, depends on the amount of water vapour in the air.

If the air is saturated there will be no evaporation and no cooling of the wet bulb, and the temperature of the two thermometers will be the same. If the air is dry there will be considerable evaporation with appreciable cooling, and the wet-bulb thermometer will register several degrees less than the dry bulb. It is, therefore, apparent that the difference between the two temperature readings bears a direct relationship to the relative humidity. The calculation of relative humidity from the temperature differences is somewhat involved, and suitable tables can be used.

Where constant references to relative humidities must be made, as would be the case in a room where the moisture of the atmosphere must be controlled, a roller-type hygrometer is recommended, as shown in Fig. 32, in which the table is incorporated in the instrument. The instrument consists of two uncalibrated thermometers, with a cursor sliding between them, and

a roller behind the cursor. To read the hygrometer, the cursor is moved until the top of it is level with the mercury in the dry-bulb thermometer, and the depression of the wet-bulb thermometer is read from the scale on the other side of the cursor. On the roller, two sets of figures appear, one above the other. The roller is rotated until the figure equivalent to the depression on the wet-bulb thermometer (in the upper series of figures) is opposite the arrow in the centre of the cursor. The relative humidity will then be recorded in the lower series of figures appearing opposite the arrow.

**Moisture Content of Textiles.**—At the beginning of this chapter it was stated that textile fibres have an affinity for moisture. The actual amount of moisture retained by a textile material will vary according to the relative

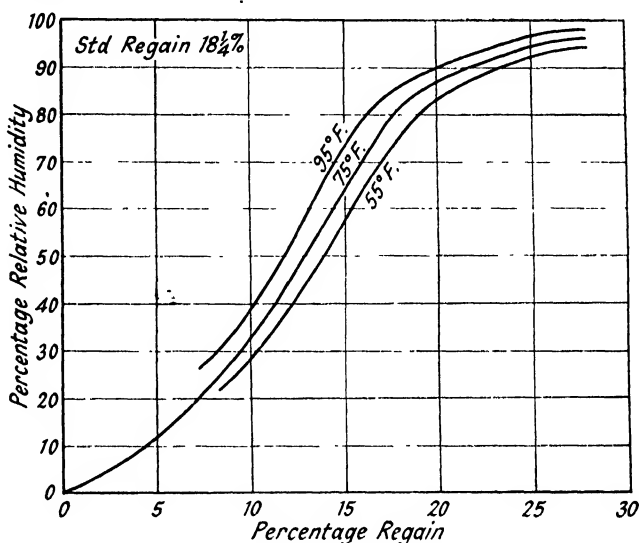


Fig. 33.—Regain Charts for Wools and Worsted.

humidity of the air. The graphs given in Fig. 33 show the amounts of water contained in wool in equilibrium with atmospheres of various relative humidities at various temperatures. It is apparent, therefore, that the weight of any batch of wool will vary from day to day as the state of the atmosphere changes.

**Nature of Fibre.**—Each textile fibre has a particular specific capacity for absorbing moisture from the air. If we were to take equal weights of absolutely dry cotton, wool, and silk, and expose them to the air and weigh them, say after twenty-four hours, they would not all weigh the same, although each would have taken up the maximum quantity of water under the given conditions. But two or more equal weights of the same fibre, *e.g.* cotton or wool, would have had the same weight after exposure. This is because the same fibre has a constant affinity for water although differing from that of the others.

For many purposes it is important not only to know how much water is included in any weight of textile material, but also to have standards for each kind of fabric. One does not want to pay for more water than is necessary; but there is no reason why one should sell textiles containing less than the recognized standard. Moreover, certain physical properties, such



as feel, count, and tensile strength, are influenced by the amount of moisture present.

We have, therefore, to know what is the standard allowance for each fibre, and to be able to determine the percentage of moisture present.

The standard allowances have been fixed by means of experiments, and are termed *regains*. These have been determined in the following manner, taking cotton as an example:

One pound of absolutely dry cotton is exposed to the air, protected carefully from access of dust, weighed at intervals over a long time, and the increases in weight are recorded. These increases will, as we have seen, vary from day to day, but if the average is taken it will work out at about 8.5 per cent. on the weight of the original dry cotton. That is, when dry cotton is exposed to air under ordinary atmospheric conditions till it has reached a state of equilibrium, it may be expected to increase in weight by 8.5 per cent. This increase is termed the *regain* for cotton.

Suppose that we had taken 10 lb. of dry cotton; after taking up 8.5 per cent. of its weight of moisture, it would weigh

$$10 + \frac{10 \times 8.5}{100} = 10.85 \text{ lb.}$$

The percentage of dry cotton present is

$$\frac{10 \times 100}{10.85} = 92.17 \text{ per cent.,}$$

and the moisture is therefore

$$100 - 92.17 = 7.83 \text{ per cent.}$$

When cotton contains these proportions of "dry" cotton and water, it is said to be at *correct condition*. In other words, when it is at correct condition the sum of the percentage dry weight and 8.5 per cent. of this dry weight is exactly 100.

It is very important to understand that when cotton is at correct-condition weight it does not contain 8.5 per cent. of water, but only 8.5 per cent. of whatever its dry weight may be.

If the sum of the percentage dry weight and the percentage regain is less than 100, the difference is due to excess of water. If the sum is greater than 100, less than the standard amount of water is present, *i.e.* the cotton is drier than is necessary. This is illustrated by Table VI.

TABLE VI.—MOISTURE IN COTTON.

Weight of Cotton tested.	Weight of Dry Cotton.	8.5 per cent. of Dry Weight = Regain.	Sum of Dry Weight + Regain = Condition Weight, per cent.	Excess of Water, per cent.
100	92.16	7.83	99.99	0.01
100	90.00	7.65	97.65	2.35
100	95.00	8.07	103.07	-3.07

The regains vary with the nature of the fibre, but they have all been fixed in a manner similar to that described for cotton. The regains for textile fibres quoted in *Textile Testing* by J. Lomax (London, 1937) are—

	Per cent.
Cotton . . . . .	8.5
Silk . . . . .	11
Viscose, cuprammonium rayon . . . . .	11
Acetate rayon . . . . .	6
Worsted yarns . . . . .	18.25
Carded woollen yarns . . . . .	17
Woollen and worsted cloths . . . . .	17
Flax and hemp . . . . .	12
Jute . . . . .	13.75

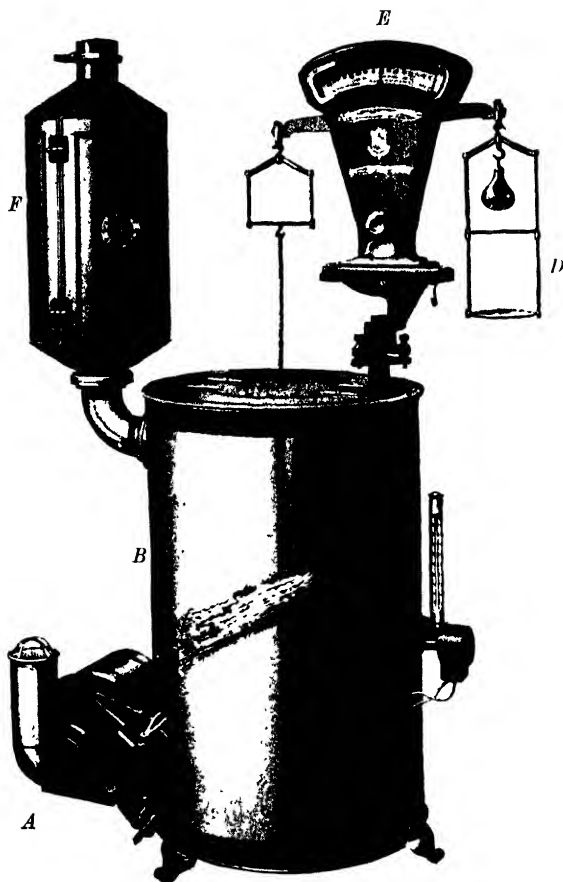


Fig. 34.—Conditioning Oven.

**Determination of Moisture in Textiles.**—On a small scale in the laboratory the percentage of moisture in a textile material may be determined in the following way:

About 5 g. of the sample is weighed out in a weighing-bottle, and then dried out in an oven for about 2 to 3 hours. The dry sample is then replaced in the weighing-bottle, the stopper inserted, and after cooling in a desiccator

again weighed. The loss in weight represents the moisture in the sample taken, from which the percentage may be calculated.

**Determination of Condition.**—In testing large quantities such as are involved in industry, a 5-g. sample could not be representative. At least 1 lb. for every 100 lb. to be tested should be taken: This 1 lb. should be taken from some twelve different parts of the batch to ensure that it is representative of the whole. Samples of 1 lb. and over are too bulky for ordinary laboratory apparatus, and special conditioning ovens are therefore used. A typical oven of this type is shown in Fig. 34.

A is a fan fitted with an electrically heated element, which blows hot air into the oven B. Inside this oven is a wire cage, which will carry up to 5 lb. of material. The cage is attached to one end of the arm of a balance, the pan for weighing being at D. Sometimes only a plain pan is provided, but on more refined apparatus such as the example shown in the figure the gross adjustment is made with the weights, and the finer variations in weight are read on an automatic scale E. The exhaust hot air from the oven passes through a chamber F. This is very useful when a number of tests are to be made in series, because the samples which will follow can be partly dried in this chamber before they enter the oven. The temperature inside the oven is maintained at 100° to 105° C.

The material to be tested is weighed—either in the cage or on a separate scale—and then entered into the oven. As it becomes lighter, weights are taken off the weighing pan until it becomes constant in weight, the weights then left on the pan representing the dry weight of the material. From the observed loss in weight the percentage moisture present can be calculated. If the “correct-condition” weight is required we proceed as follows: First calculate the percentage dry weight, then find the proper regain. The sum of these two is the percentage condition weight. From the percentage condition weight the correct-condition weight of the delivery can be ascertained. The following example will illustrate the method:

A 10-lb. bundle of cotton weighed 10.19 lb. when tested. 13 oz. 2 dr. was dried, the dry weight being 11 oz. 13 dr.

Reducing to drams, we have

$$\text{Percentage dry weight} = \frac{189 \times 100}{210} = 90.00.$$

Add 8.5 per cent. for regain,

$$\text{i.e. } \frac{90.00 \times 8.5}{100} = 7.65.$$

The sum of these weights is the percentage condition weight, i.e. 97.65.

The difference between 100 and 97.65 is the excess of moisture present. The bundle contained

$$\frac{10.19 \times 97.65}{100} = 9.95 \text{ lb. of yarn containing the correct amount of}$$

water.

Hence the shortage is 0.05 lb.

**Mixed Fibres.**—In the case of mixed fibres we must first of all know or estimate the proportion of each fibre present in 100 parts of dry material. The regain is then calculated from these proportions.

*Example.*—A yarn contains per 100 parts of dry material: cotton, 40; silk, 10; wool, 50.

The cotton contributes  $\frac{40 \times 8.5}{100} = 3.400.$

The silk contributes  $\frac{10 \times 11}{100} = 1.100.$

The wool contributes  $\frac{50 \times 18.25}{100} = 9.125.$

The total regain of the yarn is 13.625.

Claims for short weight often arise. These can be adjusted properly only if the percentage of water in the goods (condition weight) when delivered and received is known. Goods are often returned by the dyer containing less water than they might. The receiver thinks that he is getting short weight, but

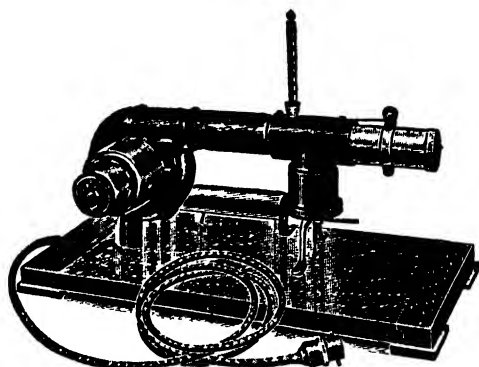


Fig. 35.—Rapid Regain Apparatus.

when the condition weight is determined this opinion may be disproved. The determination of condition weight is especially important in the case of expensive material like silk, which has also a great capacity for taking up and retaining water. It should be noted that the "condition weight" for, say, a bale of silk is a constant quantity, though the apparent weight may vary from day to day with relative humidity of the atmosphere.

The term *conditioning* is applied also to the damping of finished textile goods. There is no reason why such goods should be sold containing less than the standard allowance of moisture, especially when sold by weight or when a minimum weight per garment is required. Moreover, the finish and feel of the material are affected by the amount of moisture which it contains.

The quick determination of moisture content is becoming important for works control. In both the Dri-Sol and Woolindras unshrinkable processes the wool must be brought to an exact moisture content before it can be processed successfully. Certain apparatus is now available for making routine determinations on small samples in a few minutes. The apparatus shown in Fig. 35 consists of an air heater and a blower, which impels a stream of hot air over the sample to be tested. The temperature of the air stream is thermostatically controlled between 80° and 130° C., the exact temperature being set as desired by a small lever adjustment. After having ascertained the weight of the container, a known weight of the material is placed in it. The container is fitted to the drier, and after a period of drying at constant temperature, it is

removed from the instrument, sealed with spring caps which are provided, and weighed. The percentage regain is then easily calculated.

A more recent refinement consists of an electrical instrument which gives a direct reading of the moisture content of a textile material.' It depends on the fact that the electrical conductivity of wool varies with the amount of water which it contains.

### Count and its Determination.

Yarns are spun so that there is always a fixed relation between weight and length, or, in other words, between the weight of the original fibre and the length of yarn spun from it. This relation between weight and length is termed the *count* of the yarn or, less commonly, its *number*. It is determined by measuring carefully any given length and weighing it.

No one system of expressing counts is used universally, and there are even different systems used for the same fibre. Moreover, in some systems the weight is fixed and the length variable, while in others the conditions are reversed. In the first case the count is measured by the length of yarn necessary to make up a fixed weight, such as the number of yards to an ounce or a pound. In the second the count is the weight of a fixed length, such as the weight of 1000 yards in drams. The existence of so many systems is due to the fact that the textile industries were originally localized, and, owing to lack of means of communication, trade was restricted to narrow limits.

Expanding trade and foreign competition make the adoption of a simple and universal method very desirable. The metric system of expressing counts was recommended by a conference of experts in Paris in the year 1900, and is known as the *international system*. It is based upon a fixed weight and a variable length, the units being 1 gram and 1 metre: if 1 metre of yarn weighs 1 gram, its count is said to be 1; if 20 metres weigh 1 gram, its count is said to be 20; etc.

The principal systems of expressing counts are as follows:

*Cotton Count for Cotton Yarn and Spun Silk*.—A hank of cotton is 840 yards. The number of hanks required to weigh one pound is the count. In the case of folded yarns the count indicates the original thread before folding. Thus twofold 40's, or 2/40, means single 40-thread doubled to make 20.

*Worsted Count*.—This is based upon a hank of 560 yards, the count being the number of hanks to the pound. 2/40's means single 40's doubled to 20's.

*Yorkshire Woollen Count*.—This is based on a hank of 256 yards, the number of hanks to the pound being the count.

*Linen, Hemp, and Ramie Count*.—The hank contains 300 yards, the number of hanks to the pound being the count.

In all the above systems we have a fixed weight and a variable length. In the following methods adopted for expressing count, the length is fixed and the weight variable.

*Raw Silk Count*.—The hank or skein contains 450 metres. The weight of 450 metres in half-decigrams, i.e. 0.05-gram, is the count.

*Raw-silk Denier Count*.—The skein contains 476 metres. The weight of the skein in deniers is the count. A denier is 0.0532 gram.

*Manchester Count for Raw or Thrown Silk*.—The weight in drams of 1000 yards is the count.

**Measurement of Count**.—A suitable length of the yarn is measured off, avoiding excessive tension or slacking, and weighed on a delicate balance. A common length in the case of cotton or worsted yarns is 120 yards, but in

the case of raw silk or fine cotton 240 yards should be reeled off. Sufficient tests must be made from different hanks to obtain a fair average, and as a rule at least eight separate tests should be made on a batch under investigation. The count may be expressed as an average of these eight results. On the other hand, there is a tendency for counts to vary, and it may be desirable to work out the counts individually for each of the eight separate specimens taken, so that the degree of variation from the mean may be found. This variation is frequently a very important factor, and is often responsible for faulty garments or fabrics.

The **wrap reel** is generally used for measuring the length of yarn to be weighed in count tests. The hank is placed on a swift (Fig. 36), which is supported on brackets which allow it to rotate freely. The required length is wound off from this on a wrap reel of 54 in. circumference provided

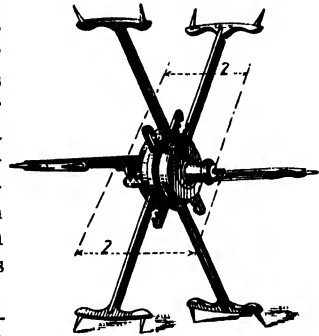


Fig. 36.—Swift.

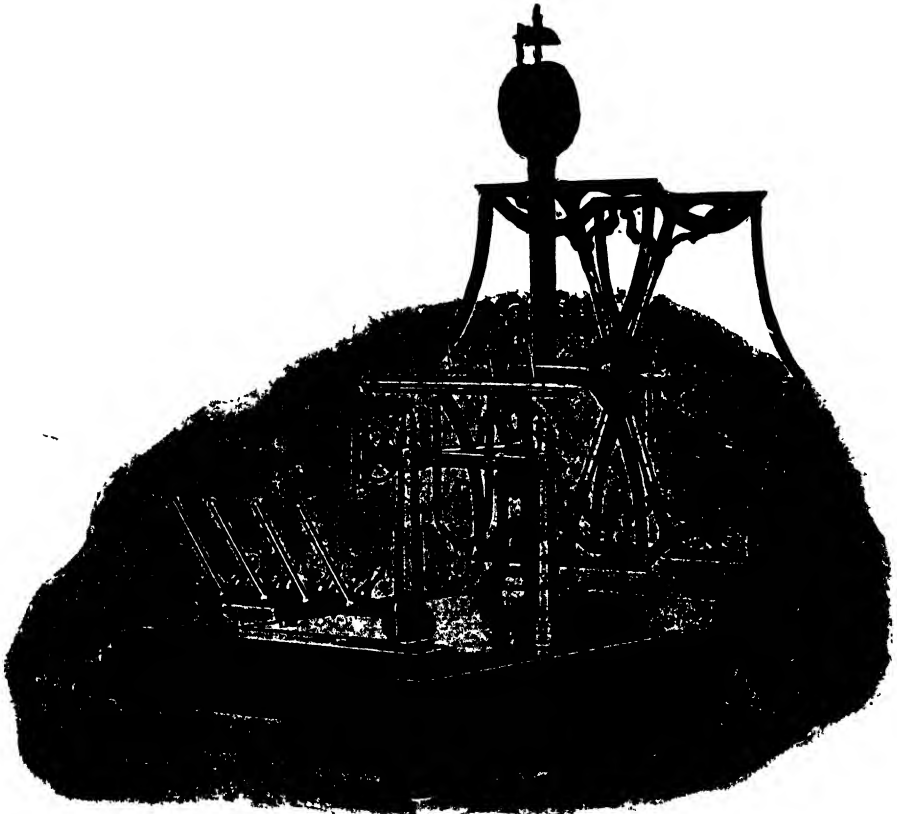


Fig. 37.—Hand Wrap Reel.

with a recording and measuring dial (Fig. 37). Each complete revolution of the pointer measures 120 yards, and is marked by the automatic ringing of a

bell connected with the recorder. The apparatus is provided also with a guide to which a transverse motion is imparted to prevent overlapping of the yarn on the reel. The base of the instrument carries a series of skewers on which cops or bobbins may be placed, and between these and the reel are glass hooks through which the yarn passes in order that uniform tension may be maintained. It is of great importance that there should be neither undue tension nor sagging of the yarn, since in either case the measurement will be inaccurate. The swift is usually supplied with a weight suspended to the axle, which exerts a certain amount of drag and thereby controls tension during winding.

When the necessary length of yarn has been measured it is removed from the reel and weighed on a balance which is sensitive to at least one-tenth of a gram, and is enclosed in a glass case. If the reeled length cannot be weighed at once it should be placed in a stoppered bottle. If left lying exposed to the air it may either lose or gain moisture, and so affect the accuracy of the test.

The actual counts are easily worked out from the figures given earlier in this chapter, quoting the relation between length and weight on which counts are based.

**True Counts.**—The weight of a given length of yarn is affected by the amount of moisture which it contains, and this, as we have seen, varies with the atmospheric humidity. Two persons testing the same yarn may obtain different results at different places or at different times, unless allowance is made for the water content. For accurate work or in cases where disputes may arise, the count should be calculated upon the yarn at correct condition. This is a constant number independent of variation in atmospheric moisture, and is known as the *true count*. The count determined without reference to the water content is the *apparent count* (count on reeling). The true count may be determined from the apparent count by dividing the latter by the percentage condition weight and multiplying by 100; *e.g.*:

Count of yarn as received	. . . . .	32.90
Percentage condition weight	. . . . .	96.50
True count	. . . . .	$\frac{32.90 \times 100}{96.50} = 34.09$

The portions measured for the test may be used to determine the percentage dry weight. They are placed in a weighing-bottle and weighed. They are then dried in a drying-oven, replaced in the weighing-bottle, and again weighed. To the dry weight then obtained the calculated regain is added. *Example* :—

Ten leas of cotton as measured weigh	190 g.
The count of the yarn as recorded is	$\frac{1000}{19} = 52.63$ .
When dry the weight was	180 g.
Adding regain	$\frac{8.5 \times 180}{100} = 15.3$ ,
$\therefore$ Condition weight is	195.3 g.
The true count is	$\frac{1000}{19.53} = 51.20$ .

Barwick (*J. Soc. Chem. Ind.*, 1913, 32, 131) tested the apparent count of the same sample of cotton yarn at intervals over three months. He found that the percentage of moisture varied from 6 to 10, while the counts ranged

from 39 to 41. He emphasized the necessity for standard conditions of humidity in testing, and of not rejecting goods for wrong count unless the tests have been made under reliable conditions.

**Oil Content.**—The true count of yarn is also affected by the amount of weighting matter or oil present. When accurate results are wanted, these must be estimated and allowed for if the true count is required. For example, it is sometimes necessary to find the true count of the original silk in a sample which has been heavily weighted.

*Example.*—The apparent count of a cotton yarn is 200. Analysis shows that the cotton contains 5 per cent. of coconut oil. Since the count is 200, the weight of 120 yards is 5 grains, and of this 5 per cent. is oil. Hence the weight of the cotton is 4.75 grains, and the count is  $1000/4.75 = 210.5$ .

If we require the true count after making due allowance for oil and moisture present, the oil should first be extracted by means of ether, and the fat-free residue dried and weighed. To this dry weight the correct regain is added. This gives the weight of the oil-free cotton at correct condition, from which the true count is obtained.

**Measurement of Length.**—It is sometimes necessary to know the length of a given weight of yarn. If a sufficient number of tests of counts have been made to give a fair average, the length of yarn in a given weight may be calculated from the count and the net weight. Thus if the count of a bundle of cotton-wool is  $31.5/2$  and the net weight 9 lb. 12 oz., the length will be  $15.75 \times 840 \times 9.75$  yards.

The direct measurement of length may be arrived at by means of a special machine made on the principle of the hank reel, but which will take ten hanks at once and measure them without overlapping. These hanks are weighed, and wound on the machine; as each is finished the machine is stopped and the length read off. From the sum of the lengths of the individual hanks, their weight, and the original net weight of the yarn, the total weight, together with the count, can be calculated.

*Example.*—A bundle of cotton weighed 9.80 lb. The hanks, weighing 1.93 lb., were measured. The sum of the individual lengths of each of the ten hanks amounted to 32,777 yards. Therefore the total length of yarn in the bundle was

$$\frac{32,777 \times 9.8}{1.93} = 166,432 \text{ yards;}$$

and the count was

$$\frac{32,777}{1.93 \times 840} = 20.22.$$

**Conversion of Counts.**—It is often necessary to convert counts expressed in one system into the equivalent in another system. There are two distinct types of conversion required in practice. Firstly, counts determined by the weight of a fixed length are to be expressed in terms of a system where the weight is fixed; and secondly, counts in which the same principle of measurement is used are to be converted.

*Converting Counts from Fixed-length to Fixed-weight Systems.*—To convert counts from a fixed-length system to a fixed-weight basis we have to multiply the length unit in yards of the known counts by the number of weight units



per lb. and divide by the product of the known counts and the length unit of the required system. For example, to convert 500-denier silk to cotton count:

520·55 yards=length unit in yards for the denier system.

8526·3 deniers=1 lb.

840 yards=length unit for cotton count.

The required figure is therefore

$$\frac{520\cdot55 \times 8526\cdot3}{500 \times 840} = 10\cdot57's.$$

In the above fraction the figures 520·55, 8526·3, and 840 are constant in every calculation required for converting denier to cotton counts, *i.e.* that part

$$\frac{520\cdot55 \times 8526\cdot3}{840} = \text{a constant} = 5283\cdot8.$$

We can therefore arrive at a constant into which the known count must be divided to obtain the desired count. These constants are given in Table VII.

TABLE VII.—COUNT-INTERCONVERSION CONSTANTS (FIXED-LENGTH AND FIXED-WEIGHT SYSTEMS).

	Cotton and Spun Silk.	Worsted.	Woollens, Yorks. Skeins.	Linen (Wet-spun).
Rayon denier and silk .	5283·8	7926	17337	14795
Rayon international .	5315	7973	17440	14882
Thrown silk . . .	304·8	457·1	1000	853·3
Jute and coarse hemp .	17·14	25·71	56·25	48

If the figures in Table VII are represented by  $K$ , the known count by  $A$ , and the unknown count by  $X$ , we can apply the following equation:

$$X = \frac{K}{A}.$$

So far only conversion of fixed-length counts into fixed-weight counts has been discussed. The same equation can naturally be used for the reverse conversion, *e.g.* of cotton counts into deniers. In this case  $X$  is known and  $A$  is unknown. Thus to convert 10·57 cotton count into denier we apply the above equation as follows:

$$10\cdot57 = \frac{5283\cdot8}{A};$$

$$\therefore A = \frac{5283\cdot8}{10\cdot57} = 500.$$

Converting counts from one fixed-weight system to another is simple; it is merely a case of multiplying by a suitable factor. These factors are recorded in Table VIII in such a way that the correct factor is found at the intersection of the horizontal row and the vertical column against which the systems involved in the conversion appear.

TABLE VIII.—COUNT-CONVERSION FACTORS (FIXED-WEIGHT SYSTEMS).

(Multiply the known counts by the factor at the intersection of required system of counting to find the equivalent counts.)

Known Counts and System.	Worsted.	Woolen (Yorks. Skein).	Woolen (West of England).	Cotton and Spun Silk.	Linen (Wet-spun), American Woolen Cut, and Fine Hemp.	Woolen (Gala- shiele).	Ramie, Cotton (Inter- national Metric).
Cotton and spun silk . . . . .	1.5	3.28	2.625	1	2.8	4.2	1.69
Worsted . . . . .	1	2.187	1.75	0.667	1.867	2.8	1.13
Woolen (Yorks. skein) . . . . .	0.457	1	0.8	0.305	0.853	1.28	0.516
Woolen (West of England) . . . . .	0.571	1.25	1	0.381	1.067	1.6	0.645
Woolen (Galashiele) . . . . .	0.357	0.781	0.625	0.238	0.667	1	0.403
Linen (wet-spun), fine hemp, American woollen cut . . . . .	0.536	1.172	0.937	0.357	1	1.5	0.605
Ramie, cotton (International metric) . . . . .	0.886	1.94	1.55	0.59	1.65	2.48	1

For example, to convert a 20's worsted count to cotton count we look under the heading "Known Counts and System" for "Worsted," and then look across the page till we find a factor under "Cotton and Spun Silk" (i.e. the unknown count and system). In this case the figure is 0.667; 20's worsted count in cotton count is therefore  $20 \times 0.667 = 13.33$ 's.

**Counts on Cloths.**—Woven fabrics are made to contain a definite number of warp and weft threads in a given area, i.e. per square inch. Thus in a cloth one may require to know (i) the number of warp and weft threads per square inch, and (ii) the actual count of the yarn used. The number of threads are determined by counting under a piece glass (Fig. 38), which has a frame exactly one square inch in area and a lens mounted above it to assist counting.

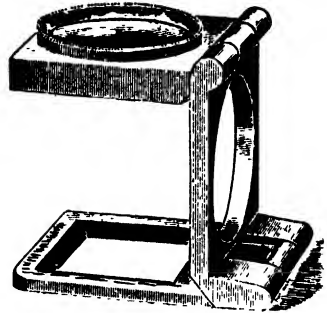


Fig. 38.—Piece Glass.

To measure the count of the yarn used in constructing the cloth a definite area, e.g. one square inch, is dissected carefully into warp and weft threads, each being collected separately and weighed. If the fabric has been starched or weighted, such addition should be removed before the test is carried out. The number of warp or weft threads dissected gives the length of yarn, and one can then from the dry weight calculate the correct condition weight and also the approximate count.

In knitted fabrics the *courses* per inch are counted under the glass along the length axis of the material, and the number of *wales* per inch along the width axis. Courses per inch give information about the tension of the yarn during knitting, which plays an important part in influencing the structure of the material. The wales per inch give relative information regarding the number of needles per inch in the machine on which the material was knitted. If the count of the yarn out of which a material has been made is required, a sufficient quantity of the yarn must be obtained by unwinding the fabric.

### Tensile Strength and Elasticity.

The *tensile strength* of a fibre or thread is expressed as the weight necessary to break it with direct longitudinal tension. In the case of piece-goods a definite area is used, and we have two different values for warp and weft. *Elasticity* is the increase in length at the breaking-point, and it is expressed as a percentage of the original length.

A yarn must have sufficient tensile strength and elasticity to withstand the strain imposed upon it by the machines used in manufacturing. The yarn must also be strong enough to allow the material into which it will be made to stand up to the conditions of wear under which it will be used. In the fabric, however, the threads give each other support, and thus a material of considerable strength can be made from yarns which are themselves too weak to withstand the strains of manufacturing. To give them strength for the weaving process such yarns are *sized*, *i.e.* treated with some strengthening agent such as starch or glue, which is washed out of the piece after it has been woven. The strength of a yarn or fabric depends, in the first place, upon the inherent strength of the fibre from which it is made. For the same fibre the tensile strength of the yarn varies inversely with the count in the case of fixed-weight counts. Other important factors affecting strength are

- (1) Length of fibre.
- (2) Fineness or evenness of diameter of the fibres.
- (3) Amount and regularity of the twist introduced in the spinning.
- (4) Physical condition of the raw fibre, *i.e.* its healthiness, state of maturity, and freedom from structural defects.
- (5) Humidity of the atmosphere.

The effects of long and short fibres and the fineness and evenness in diameter of the fibres have been referred to before (p. 63). The physical condition of the fibres is sometimes a cause of weakness. For instance, cotton grown in a cold or wet season does not ripen properly, and contains dead or immature fibres. These have much thinner walls than mature fibres, and are consequently lacking in tensile strength. Similarly, diseased or badly nourished sheep or silk-worms produce a low-grade fibre with subnormal tensile strength.

Twist has an important bearing on the tensile strength and elasticity of a yarn. Too little twist allows the individual fibres to be drawn out easily, and the yarn is consequently weak. Excessive twist reduces the elasticity, and renders the yarn less able to withstand strains. The humidity of the atmosphere exercises an important effect upon the tensile strength, which is not the same for all fibres. The tensile strengths of cotton and flax are increased by exposure to a damp atmosphere, but in the case of wool the opposite effect is produced. Table IX, showing the effect of increasing

TABLE IX.—EFFECT OF HUMIDITY ON STRENGTH OF TEXTILE MATERIALS.

Relative Humidity, per cent.	Strength of Serge, lb.	Strength of Cotton Drill, lb.	Strength of Canvas, lb.
44	186	521	599
82	160	592	729
Variation, per cent. .	- 14	+ 13.6	+ 21.7

humidity on the strength of textile fibres, is taken from the *Manchester Testing House Handbook*.

The following figures refer to a 50/1 cotton yarn tested by the authors:—

Humidity, per cent.	Tensile Strength, lbs.
67	21.6
70	24.7
72	26.4
76	26.6
87	26.8

The effect of humidity on tensile strength is of great importance in cotton-manufacturing. In the last century Lancashire became the centre of the cotton-manufacturing industry largely owing to the high relative humidity of the atmosphere in that district. Lancashire has, however, lost its unique advantage now that modern air-conditioning plants can produce any desired atmosphere in a factory.

In testing tensile strength the experiments should always be carried out under known or standard conditions of humidity, and the humidity stated in the report. Failure to do this often results in wide differences in the results obtained by different observers, particularly in the case of cotton yarns.

**Measurement of Tensile Strength and Elasticity.**—In the case of wool and cotton yarns tensile strength is expressed sometimes in pounds per lea, a *lea* being one-seventh of a hank, *i.e.* 120 yards of cotton or 80 yards of worsted. This length is measured off on a reeling machine, and then spread evenly over the two hooks of the testing machine shown in Fig. 39.

The bottom hook is moved downwards by a mechanism operated through a worm, either by hand or by an electric motor. Since the uniform rate of movement of the lower hook is a vitally important factor in testing tensile strength a motor drive is preferable. If the pull is applied by hand the greatest care must be observed to ensure that it is uniform, and that there is no jerking. The pull applied to the lea is registered on the dial. Before the dial registers anything

the lower hook will travel downwards quite a considerable distance. This represents the extension of the yarn due to its elasticity. This downward movement is recorded on a scale adjacent to the lower hook, and the

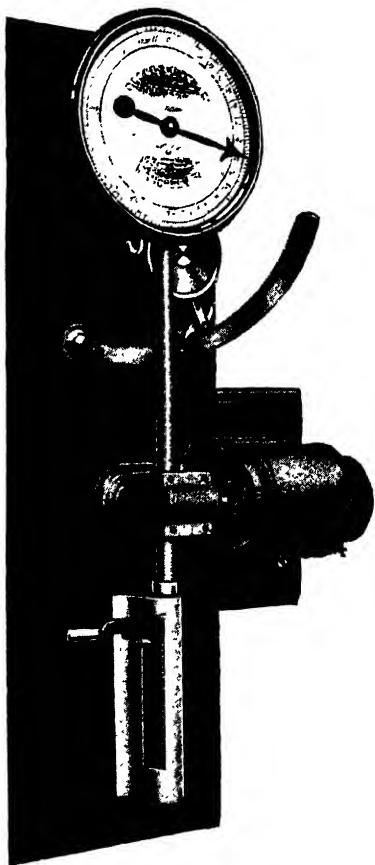


Fig. 39.—Machine for Testing Tensile Strength.

elasticity can then be ascertained. Thus if a lea 20 in. long shows an extension of 4 in., its elasticity is 20 per cent. The extension recordings on lea tests are not used much, because they are not really sufficiently reliable.

The weight needed to break the lea will be recorded on the dial, the pointer operating on a ratch so that it does not swing back when the yarn is broken, and the figure represents the tensile strength.

A breaking test recorded by this method is not the average strength of the yarn under examination but that of the weakest part.

**The Ballistic Testing Machine** is another apparatus which may be used for testing leas or strips of fabric. It differs from the machine described above in that it applies a sudden force to the sample, which approximates more closely to the majority of the conditions which apply in manufacture and wear. A ballistic testing machine is shown in Fig. 40. The heavy pendulum

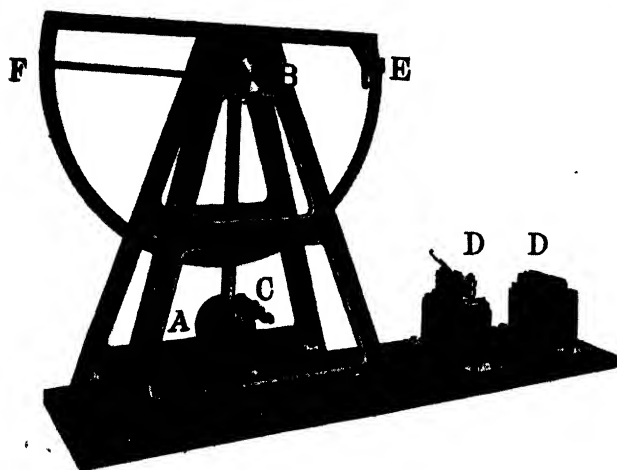


Fig. 40.—Ballistic Testing Machine.

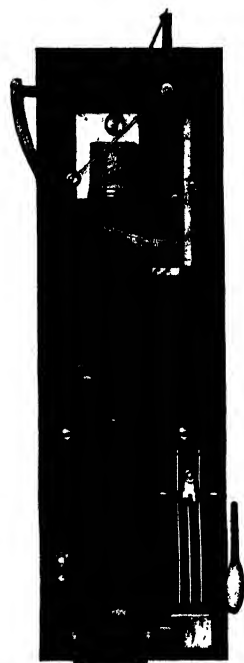


Fig. 41.—Single-thread Testing Machine.

*A* is supported by a ball-bearing at *B*. One end of the material to be tested is held in the clamp *C* on the pendulum, and the other end in the clamp *D*. Before the test is begun, the material is fixed between the clamps, and the pendulum held at *E*, at the top of its stroke, by a catch. The catch is then released and the pendulum allowed to swing. It will go through the perpendicular position before it applies any force to the sample, and it will then rise towards the position *F*, applying more and more tension to the sample all the time. When the material breaks, the pendulum will continue to rise, but the point at which it finally comes to rest is determined by the amount of energy expended in breaking the sample. When the pendulum ultimately stops moving it cannot swing back on account of a ratchet stopping device. The height to which it rises is a measure of the tensile strength of the sample. The scale is calibrated in inch-pounds.

**Single-thread Testing Machines.**—These measure the tensile strength of

single threads of yarn, and are much more commonly used than lea-testers. A typical machine is shown in Fig. 41. The tension is applied by the downward movement of the lever clamp operated preferably by an electric motor. In another type of apparatus the movement is controlled by an oil plunger. The top clamp remains stationary, and a scale calibrated in inches is placed behind it, which is connected with the lower clamp, and moves downwards with it as the yarn stretches during the test. The extension of the yarn is therefore recorded by the movement of this scale in relation to the top clamp, and the elasticity can easily be calculated. The weight applied to the yarn is recorded by the movement of a lever with a weight attached to it, which moves over a quadrant generally calibrated in pounds and ounces. This lever comes to rest when the thread breaks, and cannot swing back on account of a ratchet arrangement. The load needed to rupture the sample can therefore be read on the scale at the point where the lever comes to rest.

A further refinement, which gives a permanent record of the breaking loads and extensions of any number of tests, is the automatic recording device. A sheet of graph paper is attached to a rotating drum, which is connected to the clamp so that rotation in a clockwise direction is proportional to the extension of the yarn. An inked pen is attached to the lever in such a way that it rises as the load increases. In this way a graph of load against extension is automatically recorded as the test proceeds, the point at which the curve stops representing the breaking of the yarn. The load is recorded by the total distance covered by the curve along the vertical axis, and the extension by the length covered on the horizontal axis. On the special graph paper used the vertical lines slant to compensate for the movement of the paper with the cylinder whilst the graph is being recorded.

A typical load/extension curve as automatically plotted on a tensile-strength machine is shown in Fig. 42. Curves A, B, and C terminate at points corresponding with 12, 13.5, and 12 oz. on the vertical axis. Thus the breaking load is

$$\frac{12 + 13.5 + 12}{3} = 12.5 \text{ oz.}$$

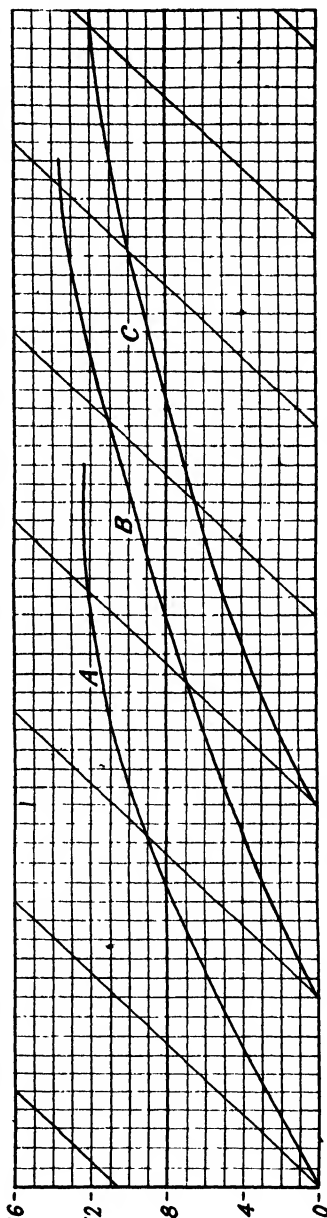


Fig. 42.—Typical Automatic Load/Extension Curves.

The curves pass through 2.75, 3.1, and 3.0 in. according to the reading taken along the horizontal axis. Thus the average extension of the yarn is

$$\frac{2.75 + 3.1 + 3}{3} = 2.95 \text{ in.}$$

**Tensile Strength of Piece-goods.**—A suitable apparatus for testing the tensile strength of piece-goods is shown in Fig. 43; it is made by Messrs

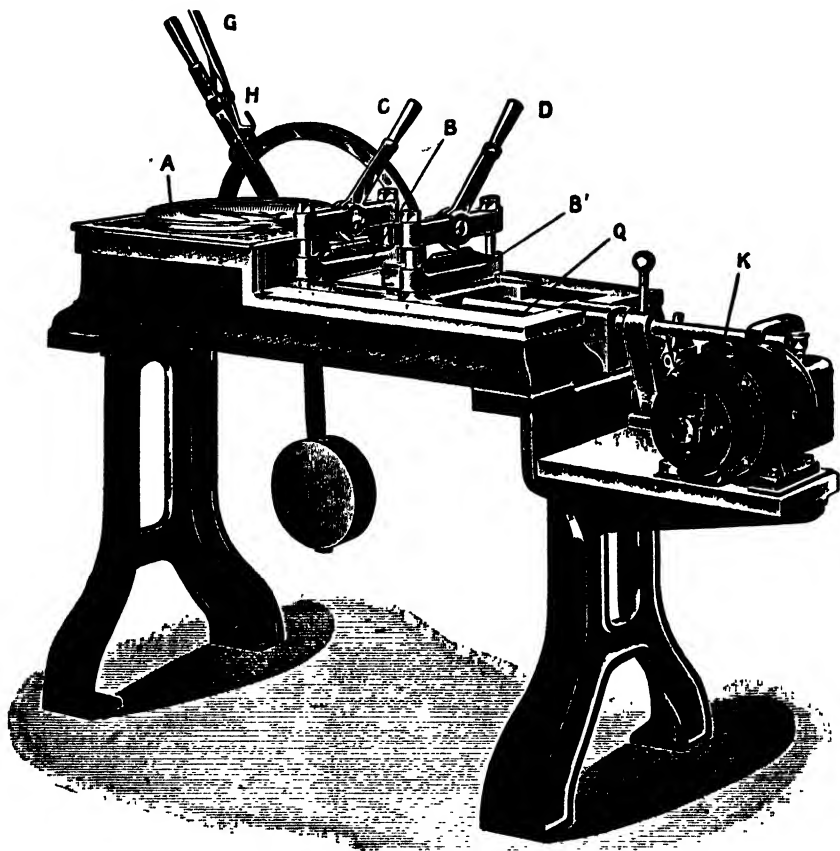


Fig. 43.—Cloth-testing Machine.

Goodbrand and Company, of Manchester. It includes a dial *A*, with divisions corresponding to actual weights and a pointer. When the material breaks, the dial pointer remains stationary, thus registering the breaking load in pounds. The pointer is set at zero by releasing the catches *G*, which set the handle *H* free, thus allowing the weight *J* to find its own centre of gravity and bring the pointer to zero. A brass plate, engraved in inches, shows the stretch of the material before it breaks. *B* and *B'* are clamps for holding the fabric to be tested; they are worked by two eccentric lever cams *C* and *D*, which are pushed over to fasten the cloth between the jaws. Between the jaws is a steel plate *E* with a brass guide bar, against which the cloth is

placed to ensure its being evenly and correctly set. Power is applied at *K* (electrically or by means of a wheel turned by hand), and is transmitted through the screw *Q* to the fabric, drawing the jaws apart till the breaking strain is reached.

**Measurement of Twist.**—The twist of a yarn is the number of complete turns which it makes in a given length, generally one inch. In dealing with

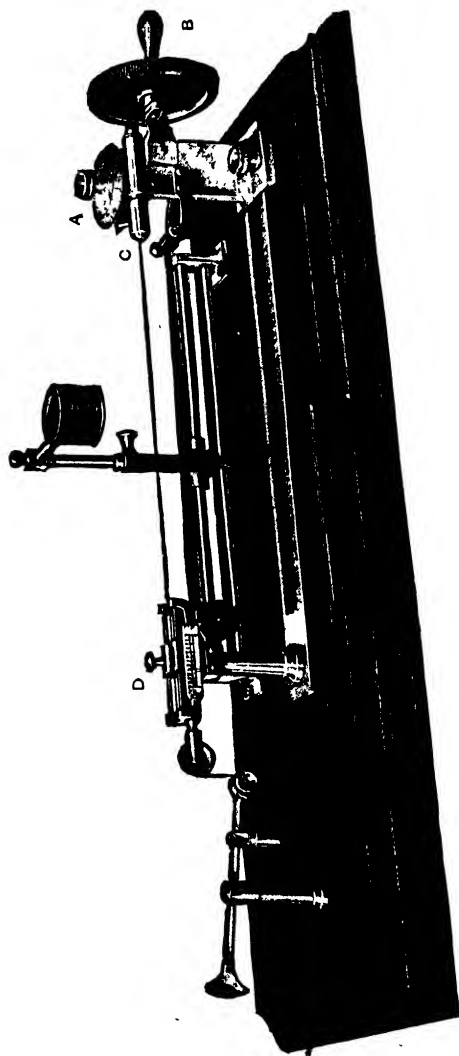


Fig. 44. --Twist-testing Machine.

folded yarns there are two twists: the twist imparted to the fibres during spinning, and that introduced in folding the single into double or threefold yarns. Twists imparted in a clockwise or an anti-clockwise direction are differentiated by the terms *S-twist* and *Z-twist*.

Considerable variations are found from inch to inch in twist, and it is only when a fairly long length such as 6 inches is tested that any approach to



regularity appears. Twist is measured by an instrument such as that shown in Fig. 44, which records the number of turns needed to untwist the fibres.

*A* is a dial which can be caused to rotate by means of a screw-crank *BC* connected with the wheel *B*. It is engraved with figures showing the number of revolutions made. The pillar is clamped to the board at any required distance from *D*. To make a test, the screw nut on the dial is loosened and the dial is set at zero. The nut is then screwed back. The yarn is fixed by means of the clamp, the pillar being moved outwards till it is just taut but

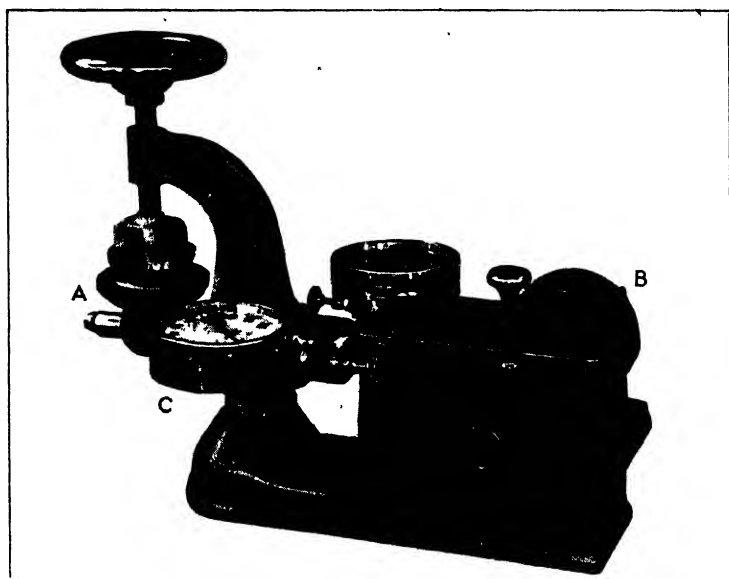


Fig. 45.—Bursting Tester.

not under undue tension. The pillar is then clamped on to the board and the handle is turned till the yarn is free from twist. The number of revolutions made is then read off on the dial. This divided by the length of yarn tested, in inches, gives the number of turns per inch.

**Bursting Test for Fabrics.**—A useful and rapid instrument for testing the strength of fabrics, which is now becoming more extensively used, is the bursting-test machine. The apparatus generally used is the Goodbrand Bursting Tester shown in Fig. 45. The fabric to be tested is firmly clamped at *A* over a rubber diaphragm, which expands as glycerin is forced into the cavity behind it when the electric motor *B* is started. As the diaphragm expands it stretches the fabric until ultimately the latter is ruptured. The pressure which has been applied is then read on the manometer *C*, and is a measure of the strength of the material.

**Wear Testers.**—Tensile strength is not the only factor of importance in determining the ability of a textile material to withstand wear. Resistance to friction is equally important, because this is always a contributory factor in determining the life of textiles. Many machines have been designed for testing wear, but the one most commonly used is shown in Fig. 46 and was designed by the Linen Research Association. The strips of fabric to be

tested are clamped between arms at *A* and *B*. The weights *C* are then attached to the bar carrying the lower clamps so that the material is kept under uniform tension. The rubbing surfaces at the lower ends of the arms *D* press against the fabric with a uniform pressure of 1.75 lb. (per sq. in.). The electric motor then oscillates the bar *EF*, which carries the upper clamps, in a horizontal direction, which causes the material to rub against the carborundum surfaces. The movement also gives distortional strain to the specimen under examination, so that wearing conditions are reproduced, where friction and distortion frequently occur simultaneously. When the fabric has worn sufficiently thin the weight *C* falls off, and this allows the arm *B* to fall, so that it puts the mechanical counter out of action. The number of rubs needed to cause the sample to break can be read on the counter, and this supplies a relative measure of the ability of the material to withstand wear.

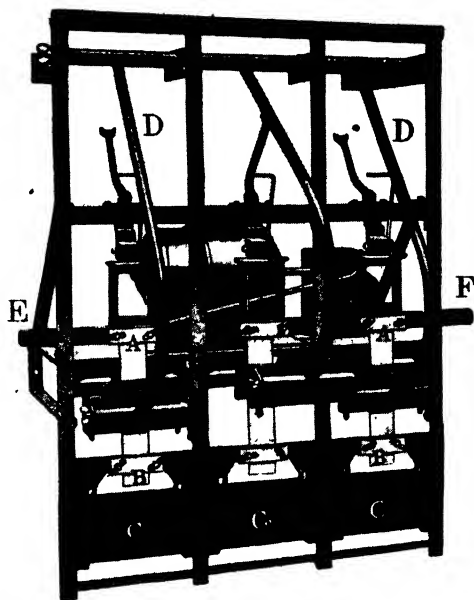
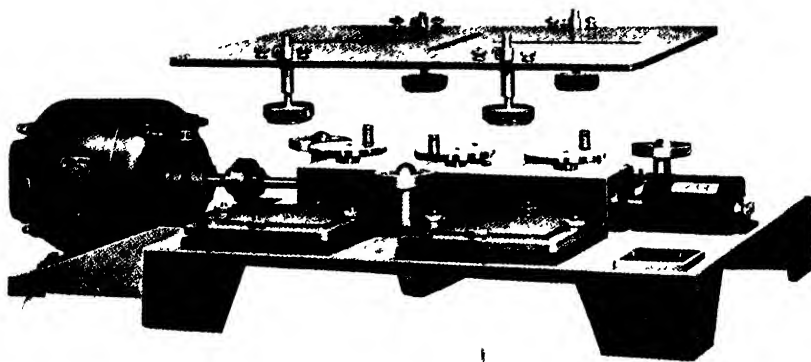


Fig. 46.—Wear-testing Machine.

Recently the Martindale Wear-Tester has been developed by the Wool Industries Research Association. The samples to be tested are held in suitable clamps attached to a bar passing through an oscillating plate. The plate



[Goodbrand &amp; Co., Ltd.]

Fig. 46A.—“Martindale” Rubbing or Wear-Tester.

oscillates in such a way that the sample to be tested is rubbed over the surface providing friction in a different direction with each movement. It is possible to use any rough material to provide the surface against which the sample is to be rubbed, but, in practice, a coarse type of cloth is generally preferred. Different weights can be attached to the clamps holding the fabric to be tested, so that the pressure of the two surfaces against each other can be modified. The resistance to wear may be assessed either by noting the number of rubs required to produce holes (a counting device is attached to the machine) or by observing the weight lost by the sample after a specified number of rubs.

### Analysis of Textile Materials.

It is frequently important to know the percentages of the impurities which a textile material contains. The following is an outline of the data to be determined and the methods used.

**Moisture.**—About 5 g. of the sample is weighed in a large stoppered weighing-bottle, and dried in an oven at a temperature of  $100^{\circ}$  to  $105^{\circ}$  C. The dry residue is replaced in the weighing-bottle, cooled in a desiccator, and weighed. The loss in weight gives the amount of water in the quantity of material taken.

**Oil.**—The dry residue after determination of moisture is placed in the receiver of a Soxhlet extractor, and extracted continuously for three hours with petroleum ether. The solvent is then evaporated on a water-bath, and the flask is dried in an oven, cooled in a desiccator, and weighed. The increase in weight of the flask gives the amount of oil extracted.

Free fatty acids in the oil may be estimated in the following way: About 25 ml. of neutral alcohol or methylated spirit is added to the flask, which is then warmed on a water-bath. The free fatty acids dissolve in the warm spirit. A drop or two of phenolphthalein is then added, and decinormal sodium hydroxide is run in carefully from a burette with constant gentle rotation, till the fatty acids are just neutralized, which will be indicated by a pink colour remaining permanently even when the flask is rotated. Each millilitre of decinormal sodium hydroxide will neutralize 0.0282 g. of oleic acid.

If it is necessary to determine the amount of unsaponifiable oil, about 5 ml. of 50 per cent. alcoholic potassium hydroxide is added to the flask, which is then connected with a vertical condenser, and heated on a water-bath for one hour to convert the saponifiable oils to soap. During this operation the contents of the flask should be mixed periodically by gentle rotation. At the end of this time the flask is removed, an equal volume of distilled water added, and the whole poured into a separating-funnel. The flask is washed out with petroleum ether, this also being poured into the separating-funnel, about 30 ml. being used. The contents of the funnel are then carefully rotated so as to bring the petroleum ether into contact with the solution without forming an emulsion. The funnel is then allowed to stand until the two layers have separated out completely, the top is opened, and the lower layer is allowed to run off into a beaker. If separation is slow, or an emulsion has been formed, some alcohol should be added. The petroleum-ether layer is washed in the separating-funnel at least three times with distilled water to remove any dissolved soap. During the first washing the funnel must be rotated gently, but afterwards vigorous shaking may be used. The washings are collected separately. The petroleum ether is finally poured into a weighed flask. The original soap solution is now returned to the separating-funnel, and again shaken with petroleum ether. This time it may be shaken vigorously, as there will be less tendency to emulsify. The petroleum layer is

separated and washed as before, and added to the weighed flask. The extraction is then repeated a third time, after which the total volume of petroleum ether is evaporated off, and the residue is weighed. If this seems excessive, it should be redissolved in petroleum ether, and washed again to remove any soap that may be present. If the previous washings have been carefully carried out, this should not be necessary. It is sometimes desirable to resaponify the residue and re-extract. It must be carefully noted that soap is distinctly soluble in petrol, especially in the presence of alkali.

**Estimation of Soap and other Matter soluble in Alcohol.**—The oil-free residue is replaced in the extractor and extracted again, using alcohol instead of petroleum ether. The residue obtained, after evaporation of the solvent, will contain soap together with any other bodies present which are soluble in alcohol. It is dried and weighed. The soap is then estimated by adding a known volume of decinormal sulphuric acid, say 50 ml., to the flask, and boiling gently to liberate the fatty acids. The contents of the flask are then poured into a separating-funnel, and the flask is rinsed twice with hot distilled water, the washings being poured also into the separating-funnel. About 25 ml. of ether are then poured into the flask to dissolve any fatty acids left, and then poured from the flask into the separator. The stopper is replaced, and the contents of the separator shaken. After standing for a short time the ether, containing the dissolved fatty acids, rises to the surface. When the ethereal layer has separated completely, the lower, aqueous layer is drawn off carefully into a beaker. The ethereal solution is washed in the separator with about 5 ml. of distilled water, which is also drawn off into the beaker. The ether is then poured through the top of the funnel into a weighed flask. The liquid in the beaker is then again extracted with ether, which is added to that already in the flask. The ether is evaporated off, and the fatty acids are dried and weighed. This gives the amount of fatty acid present as soap. If the aqueous liquid in the beaker is carefully titrated with decinormal sodium hydroxide, using methyl orange as indicator, the quantity of sodium oxide ( $\text{Na}_2\text{O}$ ) which was present as soap can be calculated, since each millilitre of decinormal acid which has disappeared corresponds to 0.0031 g. of sodium oxide. If the fatty acids are multiplied by 0.97 their equivalent of fatty anhydrides is obtained. The sum of the fatty anhydrides and the sodium oxide gives the actual amount of soap present in the material.

**Matters soluble in Water.**—The residue from the last experiment is dried, and boiled gently with distilled water for half an hour. The water is decanted into a graduated flask, and the residue is washed several times with hot water, the washings being added to the contents of the flask. After cooling, the extract is made up to the mark, and filtered. An aliquot part of it is then evaporated to dryness on the water-bath in a weighed dish, dried in the oven, and weighed.

When weighting matter is suspected, the following alternative method may also be used: The residue after extraction with alcohol is dried and weighed. It is then soaked in warm 5 per cent. hydrochloric acid for half an hour. At the end of this time it is washed with hot distilled water till free from acid, and reweighed. The soluble matter is obtained by difference.

**Mineral Matter.**—About 5 g. of the sample is weighed and incinerated in a weighed platinum or silica dish over a Bunsen flame or in a muffle, till all the organic matter has been burnt, and a white, grey, or red ash is obtained. The dish is then cooled in a desiccator, and weighed. The increase in weight gives the amount of ash. This will not necessarily be the same as the amount of mineral matter present, since some inorganic compounds, such as calcium carbonate, are decomposed by heat.

## CHAPTER IX.

### COTTON.

COTTON is the oldest and most important of the textile fibres. It has been used for thousands of years, and was found employed in America by Christopher Columbus. Cotton-spinning and cotton-weaving are two of the most important of British industries. Each cotton fibre is a unicellular hair from the seed of the cotton plant or tree. These hairs are produced by the plant to protect the young unripe seed and to assist in its distribution when mature. Each hair (or fibre), however long or short, consists of a single complete vegetable cell.

**Vegetable Cells.**—Vegetable cells vary in structure from naked masses of living protoplasm to practically empty and dead cells consisting only of cell-walls, the chief function of which is to provide support and rigidity for the plant. As a rule, they are provided with a cell-wall, which consists generally of cellulose. This is made by the living protoplasm of the cell, and laid down in layers, and as long as the cell is growing it is filled with this living protoplasm and the cell sap. Protoplasm is a jelly-like substance of very complex nature, but containing nitrogenous substances termed *proteins*, in particular one known as *plastin*.

In a young growing cell the whole cavity is filled with protoplasm and cell sap, and is distended or turgid. As a rule, part of the protoplasm is collected into a denser and more refractive nucleus, which is seen in the centre of the cell in Fig. 47.

This nucleus has some definite function in the economy of the cell, and, as a rule, division of the cell protoplasm is preceded by that of the nucleus. As the cell grows the plastin gradually forms a framework, as is seen in Fig. 48, and the empty spaces or *vacuoles* filled with cell sap make their appearance.

When the cell becomes mature the protoplasm dries up, leaving an almost empty cell. This may remain empty, be filled with cell sap, or contain the by-products of plant life. When the cell sap dries up also, as in the cotton fibre, the cell cavity retains those bodies which it held in solution as well as the remnants of the protoplasm. The cell-sap constituents include mineral salts, amino acids, sugar, and other soluble organic compounds. These remnants of cell sap and protoplasm are among the impurities which the cotton-bleacher has to remove.

**Natural History of Cotton.**—The cotton plant belongs to the natural order Malvaceæ or mallow family. It grows best in subtropical climates, and is cultivated in Asia, Africa, America, Australia, the West Indies, etc. There are

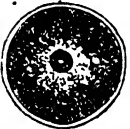


Fig. 47.

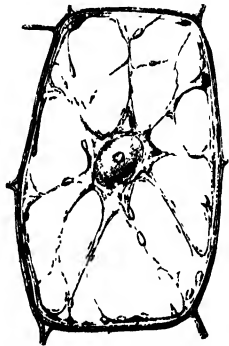


Fig. 48.—Vegetable Cells. (After Vines.)

many varieties, but according to F. H. Bowman (*Structure of the Cotton Fibre*, p. 66) the cottons of commerce belong to only four species:

*Gossypium arboreum*,  
*Gossypium herbaceum*,

*Gossypium peruvianum*,  
*Gossypium barbadense*.

*Gossypium arboreum* produces two kinds of fibres, viz. long silky and short ones. It is not largely cultivated. *Gossypium herbaceum* and a sub-variety, *Gossypium hirsutum*, are the source of most of the Indian and American cotton. *Gossypium peruvianum* produces a rough strong fibre, and is indigenous to South America. *Gossypium barbadense* produces fine silky Sea Island and Egyptian cottons. The cotton plant is perennial—that is, produces seeds year after year. But after a time the value of the cotton deteriorates, both in quantity and quality. The best results are obtained by cultivating it as an annual. This has also the advantage of enabling the cotton-grower to improve his stock by the introduction of new strains. In order to maintain a high standard of quality, constant attention is necessary to such things as proper methods of cultivation and the use of fertilizers, while many generations of selective cultivation and cross-fertilization are required to develop and make permanent a new strain. In the United States of America the ground is ploughed up during the winter, and the seed is sown in the late winter or early spring. The seeds are planted at intervals of about 18 inches in furrows which are 3 or 4 feet apart. The seedlings are thinned out if necessary, and during their growth the ground is carefully weeded. The flowers open in June, and the cotton is ripe for gathering from August to October.

The flower is succeeded by a closed pod. This contains the cotton seeds, which are wrapped up in young, actively growing hairs. When the seeds are nearly ripe the pod bursts open, and the cotton hairs project, forming a white fluffy mass. This is termed a *boll*. The fibres now complete their ripening, after which their cell contents gradually dry up, leaving the commercial cotton fibre. The drying of the cell contents, under the influence of the sun, is a very important factor in producing one of the chief properties of cotton, namely, its characteristic twist.

After the cotton has been gathered, the fibres are removed from the seeds by a process termed *ginning*. The Macarthy gin consists of a hopper containing two weighted knives called *doctors*. These work against two spirally grooved rollers covered with walrus leather, which has a rough grain and great durability. As the cotton descends the hopper it comes into contact with the revolving rollers. The doctors, pressing against these, remove the fibre, which is carried on, the seeds falling into a box beneath. The doctors are set so as just to catch the seed and leave all the short hairs on it, particularly those at the base. If the ginning is carried out carelessly some of the fibres are torn or ruptured, and little knots of short fibre are carried on with the cotton. These give rise to white opaque spots or *neps* in the yarn, which detract from its value. Under the microscope a nep is seen to consist of a mass of fibres pressed together and inextricably mixed. After ginning, the fibres will have their upper free end tapering to a point, while the basal end is open where it has been cut from the seed. Bracts, fragments of the seed coat, leaves or stem, and accidental dirt may also be present in the ginned cotton. This, after pressing into bales, is ready for the spinner. The short hairs remaining after ginning are known as *linters*. They are now removed, and are used for the manufacture of rayons. The seeds are pressed to remove the bulk of the oil. This is used for soap-making and other purposes. The residue, after pressing, forms cotton-seed cake, a valuable cattle food.

**Spinning.**—Raw cotton consists of a mass of fibres, intimately mixed, and pointing in all directions. One pound is said to contain over thirteen million individual fibres. The fibres are of different lengths, those near the base of the seed, for example, being shorter than the others. Cotton-spinning consists essentially of the following operations: (i) breaking up the raw cotton into an open mass of fibres, and at the same time removing the dirt; (ii) separating the long from the shorter fibres; (iii) laying the longer fibres parallel to one another and side by side in sufficient numbers to give the yarn the required diameter; (iv) twisting these fibres together to form a thread, and winding this thread upon a reel or bobbin. As originally carried out, by hand, the process was simpler. The fibre was opened out and fastened to a stick termed a *distaff*. The distaff was held in one hand or fastened in the spinner's belt. A spindle was then taken, and, by means of a hook at one end, a portion of the fibre was drawn out from the bundle on the distaff. This gave the drawn-out fibres an approximately parallel direction. The spindle was then made to rotate by rolling it against the body with one hand, and while rotating was allowed to fall to the ground. It was weighted with a ring, called a *whorl*, to increase the momentum of its fall. The weight of the falling spindle drew out the fibres and made them lie nearly parallel to one another, while its rotation twisted them together round a longitudinal axis, thus forming a thread. After the spindle had reached the ground the thread formed was wound on to it, and the process repeated.

In modern spinning all this is done by machines, the operation being divided into several processes. In the first or *breaking*, the cotton from the compressed bale is carried by a travelling band between fluted or spiked rollers, which pull it to small fragments. These now go to *openers and scutchers*, which consist of perforated revolving cylinders. As the cotton passes through these it is beaten by revolving blades or beaters till it is completely broken up, while at the same time a current of air draws out the impurities. The cotton leaves the scutcher through rollers, which transform it into a thick flat sheet called a *lap*. The lap then passes to the *carding* machine. This consists of cylinders covered with bent teeth or hooks, and rotating with varying velocities and on parallel axes. The lap is thus teased out into its individual fibres. These pass under combs which are set to reject the short fibres and any remaining dirt, and to lay the longer fibres in a direction parallel to one another. As the lap leaves the carding machine it passes through a ring, which tends to make the fibres more parallel to one another, and forms a loose round rope termed a *sliver*. The sliver is now drawn out on a *drawing frame*. This is made of four pairs of rollers each revolving at a greater speed than the preceding pair. The sliver passes first through the pair revolving at the lowest velocity, and in succession through the remainder with gradually increasing velocities. It is thus drawn out, to an extent depending upon the difference between the initial and final velocities. At the same time the parallel arrangement of the fibres is completed. The drawing out may be repeated, and two or more slivers may be combined and drawn out till the desired attenuation is obtained. The drawn-out sliver goes next to a *slubbing* machine, where it is still further drawn out, given a slight twist, and wound on a bobbin. Then an *intermediate frame* draws out two slubbings to the fineness of one, imparts a slight twist, and rewinds them. Still more attenuation and twist are produced by the *roving frame*, after which the rovings are ready for spinning. In cotton-spinning two methods are employed, *viz.* *throwle* and *mule* spinning. (The former is a continuous process, the roving being spun and wound on to a bobbin at the same time. It is used chiefly for the coarser yarns. Mule

spinning is intermittent, and is used for fine yarns. The roving passes between rollers which measure out a fixed quantity. At the same time these rollers are drawn out by a roving frame, to which the rotating spindles are attached. The roving is thus drawn out and spun simultaneously. The frame then travels back towards the roving bobbins, the yarn being at the same time wound on to bobbins. A mule spinning-frame is shown in Fig. 49.

**Types of Commercial Cotton.**—Cotton may be classified according to the length of its fibres or *staple*. As a general rule, other valuable properties vary directly with the length of the fibre, except that short fibres are always stronger owing to their greater diameter. A few typical cottons may be briefly described.

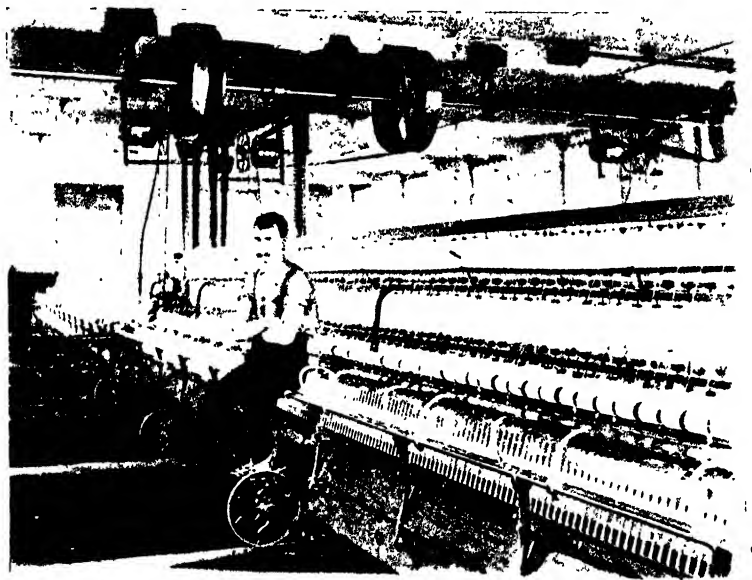


Fig. 49.—Spinning-room and Self-acting Mule.

*Sea Island Cotton.*—This is the highest and most valuable type of commercial cotton. It is grown on the coast of the Gulf of Florida, in the Barbadoes, and in other islands where soil and conditions of climate are specially adapted to the requirements of the cotton plant. The average length of the fibre is nearly two inches, and its diameter is less than that of any other cotton, *viz.*  $1/1500$  of an inch. Owing to its fineness, it can be used for spinning yarns of the highest counts, 200's to 400's. Sea Island cotton is characterized also by its evenness and its large proportion of fully ripened fibres accompanied by highly developed twist. But its most striking property, in comparison with other cottons, is its softness and highly developed lustre. Its colour varies from white to cream. There are several kinds of Sea Island cotton, such as Florida, Queensland, and Fiji.

*Egyptian Cotton.*—There are two kinds of Egyptian, *viz.* brown and white. The brown variety is finer than the white. It is, like Sea Island, very regularly developed, with but few immature or dead fibres. Its length of staple and diameter approach those of Sea Island cotton, averaging 1.5 to 1.75 inches and  $1/1500$  inch respectively. It can be spun up to 200's. The brown colour,



which is somewhat variable in depth, makes it difficult to mix this and other cottons in the unbleached condition. White Egyptian cotton is not so fine as the brown, its staple being not much more than 1 inch in length. It cannot be spun alone to a higher count than 70's. White cottons are occasionally artificially stained to resemble brown Egyptian.

*South American cotton* has a medium length of staple, from 1 inch in the lower to 1.5 inches in the highest grades. It is strong, but rather irregular and harsh. This is due, probably, to rapid drying-up. It is used alone for counts up to 70's, or mixed with other cottons of shorter staple. South American cotton has a mean diameter of 1/1300 inch.

*American cotton* is grown in the United States. There is a large number of varieties, produced by selective cultivation, some of which, such as Allamseed, Peeler, and Bender, have an average length of 1 to 1.25 inches, and are used for spinning counts up to 70's or 80's. The lower grades, such as St. Louis, average 0.9 inch in length, and are not used alone for counts much above 32's. American cotton is rather coarser than South American, its diameter averaging 1/1200 inch. It is characterized by its good colour and cleanness, and in good seasons by the regularity of its staple.

*Indian cotton* has a comparatively short staple, from 0.6 to 0.8 inch. It is suitable, therefore, for the spinning of only low counts. It is also somewhat harsh. Tinnely cotton is the most valuable variety. Indian cottons are sometimes called *Surats* after a particular variety.

*China Cotton*.—This is a good example of a low-grade cotton. The fibres are short, 0.5 to 0.7 inch, harsh, and coarse. The twist is not highly developed. It has little use except for mixing.

Table X gives a summary of the comparative properties of these varieties.

TABLE X.—PROPERTIES OF COMMERCIAL COTTONS.

Origin of Cotton.	Length of Fibre, in.	Diameter, in.	Spinning Power.
Sea Island . . . .	2 and over	1/1500	400*
Egyptian . . . .	1.5 to 1.75	1/1500	200*
South American . . . .	1 to 1.5	1/1300	70*
American . . . .	0.9 to 1.25	1/1200	70*
Indian . . . .	0.6 to 0.8	1/1200	..
Chinese . . . .	0.5 to 0.7	1/1200	..

**Grading Cotton.**—Each type of cotton has a minimum standard of quality or length of staple, and is graded upwards from this standard. In the case of American cotton the lowest grade is known as "good ordinary." This is abbreviated into the initial letters G.O. Other grades in ascending order, together with their abbreviations, are: low middling, L.M.; middling, M.; good middling, G.M.; fair good middling, F.G.M.; middling fair, M.F. These grades are readily differentiated by experts such as brokers, and are recognized by both buyers and sellers. Other varieties of cotton are not necessarily graded in the same way as American. Thus for Egyptian cotton the grades are: fair, Fr.; good fair, G.F.; fully good fair, F.G.F.; and good, G. Sea Island cotton is described as ordinary, Ord.; common, Com.; medium, Med.; good medium, G.M.; medium fine, Med. fine; fine; and extra fine.

Raw cotton is judged by visual inspection for colour, dirt, leaves, etc. Staples are then pulled out, and judged as to length and resistance to breaking with the fingers.

**Blending Cotton.**—Many yarns are made not from one particular fibre, but from blends of different varieties. By careful blending, the properties of two or more kinds of fibre can be made use of to supplement each other, to lower the cost of manufacture, or to make the resulting yarn suitable for the production of particular effects in the woven goods.

**Twist and Weft Yarns.**—With cotton the yarns for warp are generally called *twist*. Strength and elasticity are the chief qualities required. They are commonly two- or even three-fold yarns. The twist of the component threads may be in the same or in the opposite direction to that of their fibres.

Twists must be free from weak spots or knots, and must have a comparatively smooth surface. The surface of a yarn may be rendered smoother by

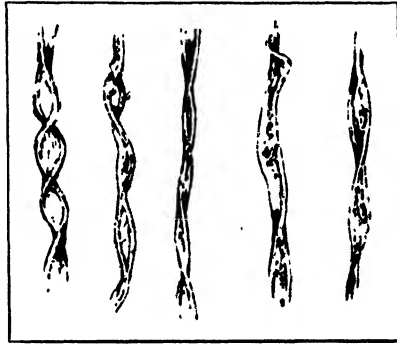


Fig. 50.—Cotton Fibres.

passing it through a gas flame or over a hot-plate to burn off the protruding fibres. This is called *gassing*. Weft yarns are spun from soft cottons. Strength and elasticity are not so important as in the case of twist. Fullness and body are the chief essentials.

**Cotton-marketing.**—Lancashire is the centre of the cotton market, and spinners buy through cotton-brokers on the Liverpool Exchange. Cotton may be bought as either (i) spot cotton, (ii) on-call cotton, or (iii) futures.

*Spot* cotton is cotton which is on the spot, and can be inspected and bought at once. *On-call* cotton is cotton selected on an agreed basis, the final price depending upon the time when the spinner requires or calls for it. Many big spinners place contracts with their brokers for the delivery of so many bales per week or per month, and a large part of this is bought "on-call." *Futures* refers to cotton purchased as a cover against loss, and such cotton generally exists only on paper. Dealing in futures is of the same nature as stock-exchange speculation, and is largely gambling on the rise or fall in price which may occur during a fixed period.

**Structure of Cotton Fibre.**—Each hair consists of a single complete elongated cell. The upper, free end tapers to a point, whilst the lower, basal end is open where it has been removed from the seed by the gin. The cell is twisted many times throughout its length, and its surface appears to be corrugated. The microscopic appearance of the cotton hair is illustrated in Fig. 50. The

diameter of the hair varies inversely with its length from  $1/1200$  to  $1/1500$  of an inch: By careful focussing, or still better by examination of a longitudinal section, four distinct parts can be made out: (i) an outer coat or cuticle consisting of cuticular cellulose; (ii) a thick cell-wall built up of layers of ordinary cotton cellulose; (iii) an inner layer of cuticular cellulose; and (iv) a cavity or lumen containing the dried cell contents. These are seen in Fig. 51, taken from a paper by de Mosenthal (*J. Soc. Chem. Ind.*, 1904, 23, 292).



Fig. 51.—Longitudinal Section of Cotton Fibre.  $\times 1000$ .

The outer cuticle of "cuticular cellulose" is insoluble in cuprammonium solution. The surface appears to be striated, which according to de Mosenthal (*loc. cit.*) is due to rows of stomata.

The cell-wall consists of normal cotton cellulose, which dissolves readily in cuprammonium solution. In a well-developed hair the cell-wall constitutes about 90 per cent. of the fibre. It has a stratified structure, the innermost layer being formed last. A diagrammatic representation of the cell-wall is

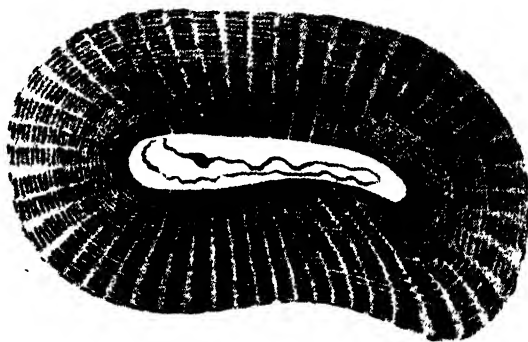


Fig. 52.—Cell-wall of Cotton Fibre.

seen in Fig. 52, which is taken from a paper by Slater (*J. Soc. Dyers Col.*, 1927, 43, 182).

The inner layer is similar in nature to the outer cuticle, both consisting of cuticular cellulose. These cuticles can be observed by mounting a hair in Schweitzer's solution. The cuticles do not dissolve in this reagent, but the cell-walls swell up and finally dissolve. The rapid swelling of the cell-wall causes the cuticle to be ruptured in places, and the swollen cell-wall protrudes through the ruptured cuticle forming globular swellings (Fig. 53). The inner cuticle also remains undissolved, thus making the lumen plainly marked.

The ruptured cuticle can be seen wrapped round the hair between two successive swellings.

The characteristic twists or convolutions are developed during ripening. They may be either right- or left-handed. According to Slater (*loc. cit.*), if a

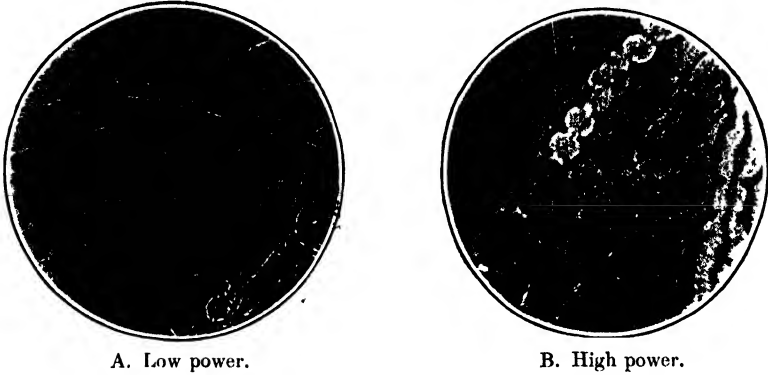


Fig. 53.—Globular Swellings of Cell-wall.

cotton hair is mounted in caustic soda solution it will appear to have a basket-work structure, which is not a mesh of crossing threads, but a true spiral structure produced by the spirals in the wall on the upper side of the hair coming into focus with those in the wall on the lower side. This is seen in Fig. 54.

The convolutions in a fully ripened hair vary from 200 to 300 per inch. The twist is more marked in some fibres than in others, and the number varies

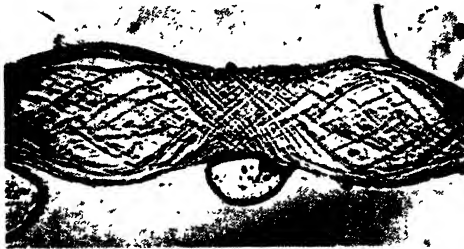


Fig. 54.—Spiral Structure of Cotton Hairs, showing Fibrils.

with the type of cotton. They are, for example, more numerous in Sea Island than in American cotton. In the majority of the hairs one finds a well-developed twist, thick cell-walls, and a clearly marked lumen. These are fully matured fibres. Sometimes there is comparatively little twist, accompanied by rather thin cell-walls and a somewhat indistinct lumen. Fibres showing these characteristics are unripe, or only partly matured. In others the twist may be entirely absent, the cell-walls extremely thin, and the lumen collapsed and invisible, the fibres looking like flat pieces of slightly twisted tape. These are known as *dead* fibres. All cotton contains a few dead and unripe fibres, but, under favourable conditions of growth, the number is small. Bad seasons, overcrowding, neglect of cultivation, and worn-out plants are among

the conditions which increase the numbers of immature or dead fibres. They are more common at the base of the seed than on other parts. If the proportion is large the cotton is poor in quality.

The appearance of these fibres is shown in Figs. 55 and 56. In Fig. 55 different stages of development are visible from fully matured to dead fibres. Fig. 56 shows a number of fibres in transverse section. In the well-ripened fibres the lumen is quite distinct, and the cell-walls are thick. In unripe fibres the lumen is either indistinct or absent, and the cell-walls are comparatively thin. These unripe fibres may be rendered easier to detect by treating the sample with Schweitzer's solution before examination. Dead and unripe fibres have comparatively little or no cuticle, and are often devoid of

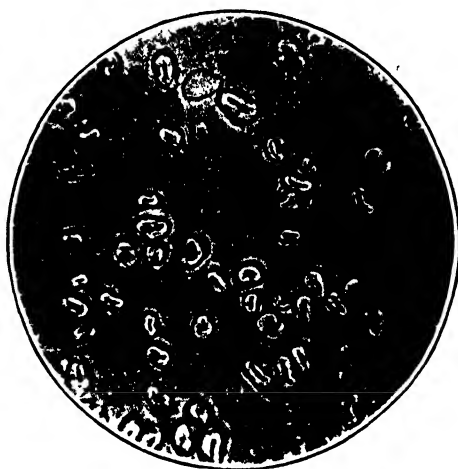
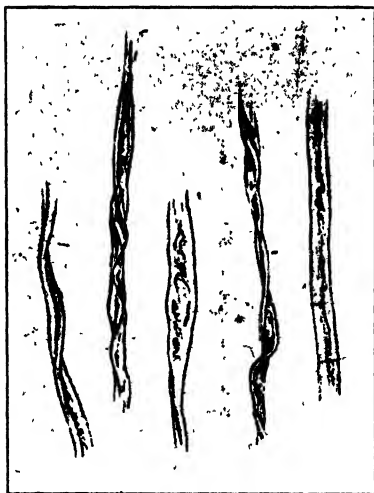


Fig. 55.—Ripe, Unripe and Dead Fibres.

Fig. 56.—Cross-sections of Ripe and Unripe Fibres.

twist. Hence they do not give globular swellings like ripe fibres with a well-developed cuticle. When treated with zinc chloriodide solution, unripe and dead fibres develop the colour much more slowly than ripe ones. A solution of iodine in potassium iodide colours ripe fibres dark brown and unripe ones yellow. In a solution of sodium hydroxide of 18 per cent. concentration, unripe fibres retain their twist and become only lighter and more transparent. Unripe and dead fibres appear purple or dark blue when examined by polarized light, lying at  $40^\circ$  to the axis of a selenite plate in a polarizing microscope, and become yellow or orange when rotated through  $90^\circ$ . Ripe fibres give yellow to yellowish-green before and after rotation through  $90^\circ$ . Unripe or dead fibres occur frequently in small bunches or clusters, forming *neps*. The appearance of a *nep* is illustrated in Fig. 57.

If *neps* are not removed from the cotton before spinning they become incorporated in the yarn, giving rise to *motes*. *Neps* are more common in fine than in coarse cottons, since the former have a relatively thin secondary wall. Also some environments produce more than others, as do some varieties. Thus Sea Island cottons are bad in this respect, as also are West Indians.

Unripe fibres and *neps* are one cause of trouble in cotton-dyeing. With direct dyes they are dyed a deeper shade than ripe fibres. With basic dyes

on a tannin-antimony mordant, unripe hairs are dyed only in the interior, while ripe ones are dyed homogeneously. With alizarine, para-red, and indigo, neps show up as light-coloured streaks or patches (*Memoirs of the Shirley Institute*, 1923). Neps give also bad results when mercerized, though mercerization increases to some extent their affinity for dyes. Light patches or streaks may be caused in dyed cotton goods also by groups of fibres which are not so thin-walled as to form neps in the spinning process, but which are too thin to exhibit the full development of colour. Neps not only occur in unspun cotton, but are formed also during the spinning process, since flabby, thin-walled hairs, which offer little resistance to bending stresses, easily become rolled up into tangled masses.

**Constituents of Cotton.**—Raw cotton contains, in addition to cellulose, the usual constituents of a vegetable cell. These include (i) oil and wax, (ii) pectoses and pectins, (iii) proteins and simpler nitrogen compounds, (iv) organic acids, (v) mineral matter, (vi) colouring matter, and (vii) water.

Cotton yarns, or piece-goods, may contain also dirt, size, or oil collected during manufacture. There is but little accurate information as to the exact proportions in which these constituents are present, with the exception of cellulose. Perhaps the approximate composition of raw cotton may be taken as—

	Per cent.
Cellulose . . . . .	85.5
Oil and wax . . . . .	0.5
Proteins, pectoses, and colouring matters . . . . .	5.0
Mineral matter . . . . .	1.0
Water . . . . .	8.0

The properties of these constituents of cotton must be described briefly.

### Cotton Oils and Waxes.

The oils and waxes of cotton consist of

- (1) Glycerides or readily saponifiable fats and oils.
- (2) Waxes.
- (3) Unsaponifiable oils.
- (4) Free fatty acids.
- (5) Traces of soaps.

The total quantity of oil *plus* fat which can be extracted from cotton is somewhat variable, and depends upon (i) the nature of the solvent, (ii) the

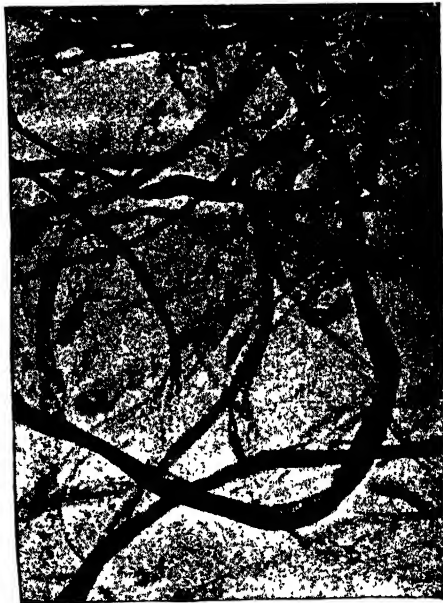


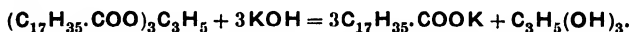
Fig. 57.—Nep.

temperature of extraction, and (iii) the physical condition of the cotton. Chloroform is the best solvent to use. Clifford, Higginbotham, and Fargher (*J. Text. Inst.*, 1924, 15, r 131) obtained 0.75 g. from 100 g. of cotton. Fargher and Probert (*J. Text. Inst.*, 1923, 14, r 49) investigated the fatty matter obtained by extracting two tons of cotton. They found palmitic, stearic, and oleic acids but no glycerol. This indicates that only waxes can be present. The crude wax was found to contain the following monohydric alcohols:—

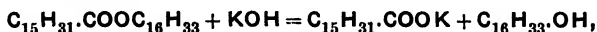
Montanyl alcohol . . . . .	$C_{28}H_{57}.OH$
Carnaübyl alcohol . . . . .	$C_{24}H_{48}.(OH)_2$
Sitosterol alcohol . . . . .	$C_{27}H_{45}.OH$
$\alpha$ - and $\beta$ -Amyrin . . . . .	$C_{30}H_{49}.OH$

The principal constituent was a new alcohol, which the authors termed *gossypyl alcohol*, having the formula  $C_{30}H_{61}.OH$ . This exists in three forms, with melting-points (i)  $87^\circ$  to  $88^\circ$  C., (ii)  $86^\circ$  C., and (iii)  $82^\circ$  to  $83^\circ$  C. Small quantities of two crystalline hydrocarbons were isolated also, *viz.* triacontane,  $C_{30}H_{62}$ , and hentriacontane,  $C_{31}H_{64}$ , and in addition to these a liquid hydrocarbon with a high boiling-point.

The difference between a fat and a wax may be referred to briefly. A *fat* is a triglyceride of a solid fatty acid, such as stearic acid. When heated with an alcoholic solution of potassium hydroxide it is decomposed or *saponified*, giving the potassium salt of the fatty acid (soap) and glycerol in accordance with the equation:



A *wax* is very difficult to saponify, but when heated with alcoholic potassium hydroxide solution under pressure it is decomposed, giving the potassium salt of the fatty acid and a solid monohydric alcohol. Thus in the case of spermaceti the reaction is



the products of saponification being potassium palmitate and cetyl alcohol. Although waxes are difficult to saponify, they can be emulsified by means of a hot aqueous solution of soap. Hence when cotton is boiled with caustic soda solution, and any saponifiable oil which is present is changed into soap, the solution of soap formed emulsifies the wax. Moreover, the waxes are saponified to a certain extent by prolonged heating with caustic soda under pressure. The waxes appear to be essential to cotton-spinning. When they are removed, before spinning, the cotton loses tensile strength, and is difficult to spin. Their high melting-points explain the necessity for a warm, moist atmosphere in spinning. The difficulty of removing them from cotton goods during bleaching is a common cause of trouble, since they are all highly coloured.

### Nitrogenous Constituents of Cotton.

These consist of (i) proteins, (ii) amino acids, and (iii) complex nitrogenous compounds associated with the colouring-matter which, unlike proteins and amino acids, cannot be removed by means of alkali.

**Proteins** are complex organic compounds associated with living animal and vegetable matter. They are, as a rule, colourless, amorphous substances, having a high molecular weight and all the properties of typical colloids. They contain the following elements: carbon, hydrogen, oxygen, nitrogen, and sometimes sulphur and phosphorus. The molecular weight of proteins is

unknown, but is probably not less than 15,000. They are associated in Nature with other bodies, such as amino acids and salts, from which they can be separated by dialysis on account of their colloidal properties. The approximate composition of proteins is—

	Per cent.
Carbon . . . . .	50 to 55
Nitrogen . . . . .	15 to 19
Hydrogen . . . . .	6.9 to 7.3
Oxygen . . . . .	19 to 24
Sulphur . . . . .	0.3 to 3.1
Phosphorus . . . . .	0.4 to 0.8

*General Properties of Proteins.*—Some proteins are soluble in water, others are insoluble. When they dissolve in water they are generally coagulable by heat. All proteins dissolve in a solution of sodium hydroxide, but in some cases, e.g. wool, solution is accompanied by decomposition. The protein is precipitated from the alkaline solution by neutralizing with acid. Proteins are precipitated from their aqueous solutions by saturation with certain salts, such as sodium sulphate or ammonium sulphate. Their aqueous solutions are optically active and have all the properties associated with colloids. Proteins are insoluble in organic solvents, and can be precipitated from aqueous solutions by adding excess of alcohol.

*Identification of Proteins.*—The coagulation of proteins by acids forms a delicate test for their recognition, since neutral or faintly acid solutions are generally coagulated when boiled. The presence of alkali inhibits the reaction. Nitric acid is a sensitive reagent for this reaction, and its delicacy is increased by the presence of sodium chloride or magnesium sulphate. The test may be carried out in the manner described by Allen (*Commercial Organic Analysis*, 5th edition, 4, 53). Five volumes of a saturated aqueous solution of magnesium sulphate are mixed with one of nitric acid (sp. gr. 1.42). Some of this mixture is placed in a test-tube, and a solution of the protein is poured carefully on to its surface. An opalescent zone is produced immediately at the junction of the two liquids.

Proteins are precipitated from their solutions by many other reagents, including the following:—

(1) *Tannic acid.* This reaction takes place in a neutral solution, or one containing a weak organic acid. If a mineral acid be present, sodium acetate should be added. Almen's reagent is commonly used; it is made by dissolving 4 g. of tannic acid in 190 ml. of 50 per cent. alcohol, and adding 8 ml. of 25 per cent. acetic acid. Tannic acid also precipitates peptones, gelatin, and starch. Phenol acts in a similar manner to tannic acid.

(2) *Picric acid* precipitates proteins completely from a neutral solution or one acidified with acetic acid. In the latter case mucin is thrown down also. Peptones also are precipitated, but the precipitate redissolves on warming the mixture.

(3) *Potassium ferrocyanide* produces a flocculent precipitate with proteins in the presence of acetic acid. Peptones and gelatin are not thrown down. This reaction is made use of in the clarification of vinegar.

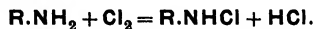
(4) *Phosphomolybdic acid* and *phosphotungstic acid* precipitate all proteins.

(5) *Salts of many of the heavy metals* precipitate proteins from their solutions as albuminates, consisting of the protein in combination with the oxide of the metal. If the precipitate be treated with sulphuretted hydrogen, the protein can be recovered unchanged. Copper sulphate in a neutral



solution or in one acidified slightly with acetic acid precipitates proteins completely on warming.

(6) *Chloramine reaction*. When a solution containing a protein is treated with chlorine-water, or a hypochlorite and acid, an insoluble compound termed a *chloramine* is formed:



Chloramines are unstable bodies, which decompose gradually on drying with liberation of chlorine. They sometimes cause tendering in bleached cotton if proteins are not completely removed during preliminary scouring.

*Colour Reactions of Proteins*.—Proteins may be identified by means of certain colour reactions. These, however, are generally given also by other bodies of similar constitution, *i.e.* which contain amino groups. The chief of these are—

(1) *Millon's reaction*. When a solid protein is warmed with a little Millon's reagent a red colour is produced. Solutions give at first a white precipitate, which becomes red when warmed. Other bodies containing an amino group attached to an aromatic radical all give the same reaction. The reaction is really a test for tyrosine. Gelatin does not give any coloration.

Millon's reagent is prepared by treating mercury with an equal weight of nitric acid of 1.4 specific gravity and diluting the solution with twice its volume of cold water. It consists of a solution of mercurous nitrate containing nitrous acid. A similar reagent, consisting of an acid solution of mercuric nitrate, is made by dissolving mercury in twice its weight of nitric acid.

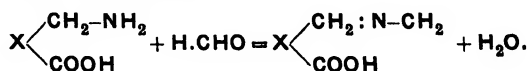
(2) *Liebermann's reaction*. Solid proteins dissolve when heated with concentrated hydrochloric acid, giving a violet solution which changes on further heating to reddish-brown or brown.

(3) *Xanthoproteic reaction*. Practically all proteins when treated with concentrated nitric acid give rise to a yellow compound, termed *xanthoproteic acid*. This becomes orange when treated with ammonia.

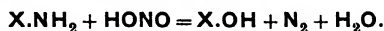
(4) *Biuret reaction*. If a few drops of a dilute solution of copper sulphate are added to one containing a protein, and then an excess of sodium hydroxide, the liquid after the precipitate has settled will have a deep bluish-violet or violet colour.

*Action of Enzymes and Bacteria*.—Most proteins are decomposed by bacteria, and in some cases offensive odours are produced, in others coloured products. All proteins are attacked by proteolytic enzymes.

*Action of Formaldehyde*.—When a protein is treated with formaldehyde, condensation with an amino group takes place with the formation of an insoluble compound, of the type:



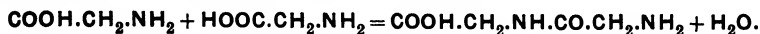
*Action of Nitrous Acid*.—Nitrous acid reacts with the amino groups of a protein, replacing them by hydroxyl groups:



*Amphoteric Nature of Proteins*.—All proteins contain amino and carboxyl groups, and like amino acids are amphoteric, *i.e.* have the properties of both acids and bases. In the presence of acids they act as bases, and in the presence of bases as acids. In every case, however, there is some particular hydrogen-ion concentration, termed the *iso-electric point*, at which it combines with neither acid nor base. For silk this is *pH* 3.2, for wool *pH* 4.8. This means

that at pH 3.2 silk has neither acidic nor basic properties. On the acid side of pH 3.2, e.g. 3.0, silk acts as a base, whilst on the alkaline side of pH 3.2, e.g. 4.0, it acts as an acid.

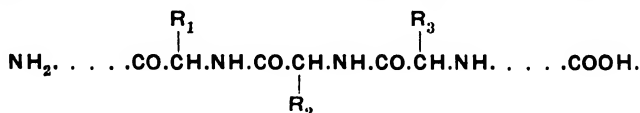
**Chemical Nature of Proteins.**—Proteins are built up in Nature by the condensation of a number of molecules of the same or different amino acids with the elimination of water. When two molecules of aminoacetic acid are condensed the following reaction takes place:—



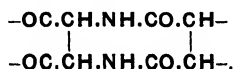
The compound  $\text{COOH.CH}_2\text{.NH.CO.CH}_2\text{.NH}_2$  is still an amino acid, and can be condensed with a third molecule of aminoacetic acid to give the compound:



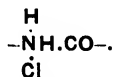
By continuing this process, a long chain known as a *peptide chain* can be obtained, the typical grouping of which is  $-\text{NH.CO.CH}_2-$ . Thus, a protein consists essentially of a chain of these  $-\text{NH.CO.CH}_2-$  groups with free carboxyl and amino groups at either end. An hydrogen atom of the  $-\text{CH}_2$  group may condense also with an amino-acid residue (R), giving



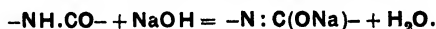
In some cases these peptide chains may be connected by cross-linkings, thus:



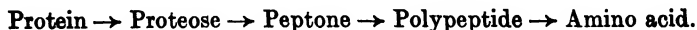
These facts explain the amphoteric nature of a protein. When treated with an acid the free amino group is neutralized, giving a hydrochloride,  $\text{R.NH}_2\text{.HCl}$ . The  $-\text{NH.CO}-$  group reacts also with acids, to give with hydrochloric acid



Alkalis first neutralize the carboxylic group, giving  $-\text{COONa}$ , and then react with the  $-\text{NH.CO}-$  group in the following manner:—



**Hydrolysis of Proteins.**—When a protein is hydrolysed it is resolved gradually into the amino acids from which it was formed. Hydrolysis can be effected by boiling with solutions of acids or alkalis, and also by the action of proteolytic enzymes. The change occurs in stages, which may be represented thus:



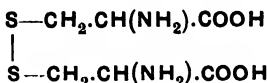
**Proteoses**, like proteins, are still colloids, but the molecular complexes are smaller. Their solutions are not coagulated when heated, but are precipitated when saturated with ammonium sulphate. They give the general reactions of proteins.

**Peptones**, produced by the hydrolysis of proteoses, are readily soluble in water and are diffusible—that is, they are no longer colloids. Their solutions are not coagulated by heat, nor precipitated when saturated with ammonium sulphate. Like proteins they form insoluble precipitates with tannic acid.

**Polypeptides** may be regarded as simple peptones having a comparatively low molecular weight. They resemble the peptones in general properties. They are of interest on account of the fact that they can be prepared in the laboratory, and indicate the manner in which proteins are formed in Nature from amino acids. A polypeptide containing eighteen amino-acid residues was prepared by Emil Fischer.

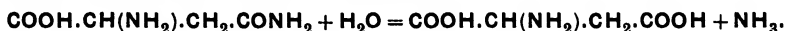
**Amino Acids.**—All proteins, as stated above, can be resolved by hydrolysis into simple amino acids, but they do not necessarily yield the same acids. The commoner ones are—

Glycine (aminoacetic acid)	$\text{NH}_2\text{CH}_2\text{COOH}$
Alanine ( $\alpha$ -aminopropionic acid)	$\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$
Valine ( $\alpha$ -amino- <i>isovaleric</i> acid)	$(\text{CH}_3)_2\text{CH}\cdot\text{CH}(\text{NH}_2)\text{COOH}$
Cystine (disulphide of thioserine):	



Serine ( $\alpha$ -amino- $\beta$ -hydroxypropionic acid)	$\text{HO}\cdot\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
Lysine ( $\alpha,\epsilon$ -diaminocaproic acid)	$\text{NH}_2\text{CH}_2\cdot(\text{CH}_2)_3\text{CH}(\text{NH}_2)\text{COOH}$
Phenylalanine	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
Tyrosine ( <i>p</i> -hydroxyphenylalanine)	$\text{OH}\cdot\text{C}_6\text{H}_4\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$

**Acid Amides.**—Asparagine,  $\text{COOH}\cdot\text{CH}(\text{NH}_2)\text{CH}_2\text{CONH}_2$ , which is an amide of aspartic acid, is a common constituent of vegetable tissues, and is present in cotton. When boiled with acid or alkali it is hydrolysed, with the formation of aspartic acid and ammonia:



**Colouring-Matters.**—The colouring-matters of cotton are associated partly with the waxes, proteins, and pectins, and are removed with these. There is, however, a residuum, which can be removed only by bleaching with an oxidizing bleaching agent, such as bleaching powder. Little is known of the constitution of these substances, but they appear to contain nitrogen.

### Pectoses and Pectins.

Pectose is a colloidal substance belonging to the group of chemical compounds termed *carbohydrates*. It has the same formula as cellulose, *i.e.* some multiple of  $\text{C}_6\text{H}_{10}\text{O}_5$ . This is expressed by the formula  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ . It occurs associated with cellulose in the cell-walls of vegetable cells and in various fruits. It differs from cellulose in being soluble in boiling alkalis and insoluble in Schweitzer's solution. When pectose is boiled with sodium hydroxide it is changed into a soluble body termed *pectin*,  $\text{C}_{32}\text{H}_{40}\text{O}_{28}$ , which is the chief constituent of Irish and Iceland mosses. The same change is produced by a ferment occurring in plants known as *pectase*. Thus, both pectoses and pectins occur simultaneously. Pectin dissolves in hot water, and when the solution is cooled a jelly is formed. This is seen in many kinds of jam and in the jelly obtained by boiling Irish moss with water. Pectin can be precipitated from its solutions by means of basic lead acetate. If pectin be boiled with water for a long time it is changed into another substance, *parapectin*, and finally into *metapectin*. When boiled with alkalis pectin is decomposed, gradually giving rise to the sodium salt of an acid termed *pectic acid*,  $\text{C}_{16}\text{H}_{22}\text{O}_{15}$ .

If this solution is acidified, insoluble pectic acid is precipitated or forms a jelly according to the concentration of the solution. Pectic acid is produced also from pectins by the action of ferments, and hence is found also in vegetable tissues. It is thought that calcium or magnesium pectate plays a part in cementing together the cells of woody tissues. Both salts are insoluble in water. Still further boiling with alkali finally changes pectic acid into the less complex sodium metapectate. The solution of this salt does not give a precipitate with acids, *i.e.* metapectic acid is soluble in water. Moreover, it is no longer a colloidal substance. Thus, when pectoses, pectins, or pectates are boiled with an alkali, the final product is soluble, diffusible sodium metapectate.

### Mineral Matter.

The nature and amount of mineral matter found in cotton varies with the composition of the soil in which it is grown. Certain elements are essential to plant life. In addition to carbon, hydrogen, nitrogen, oxygen, and sulphur, small quantities of calcium, magnesium, sodium, potassium, iron and phosphorus are necessary. Silica is required also to give rigidity to hard tissues.

The exact nature of the mineral matter in cotton cannot be determined directly. All that can be done is to burn the tissue to an ash, and determine the acids and bases present. There is a difficulty in connection with this process: some of the bases are combined with organic acids, and when ashed give carbonates. Thus, the presence of carbonate may merely indicate that an organic acid was originally present. The proportion of ash obtained from raw cotton is usually between 1 and 2 per cent.

### Cellulose.

Cellulose,  $(C_6H_{10}O_5)_n$ , is the essential constituent of all vegetable tissues, and belongs to the group of chemical compounds known as carbohydrates. It may be prepared from cotton in the following manner: The oil and wax are removed by extraction with boiling chloroform. The proteins and pectins are dissolved by boiling with dilute sodium hydroxide solution and washing with water. The washed residue is treated with chlorine-water to oxidize colouring-matters, washed, and soaked in dilute hydrochloric acid to dissolve mineral matter. It is then washed thoroughly with water and dried.

**Varieties of Cellulose.**—There are several types of cellulose, the chief of which are—

- (1) Normal cellulose of cotton, flax, and ramie.
- (2) Hemicellulose, which is less resistant to hydrolysis by acids and alkalis than normal cellulose.
- (3) Lignocellulose, found in jute and woody tissues.
- (4) Cutocellulose and adipocellulose, associated with cuticular and suberized tissues.

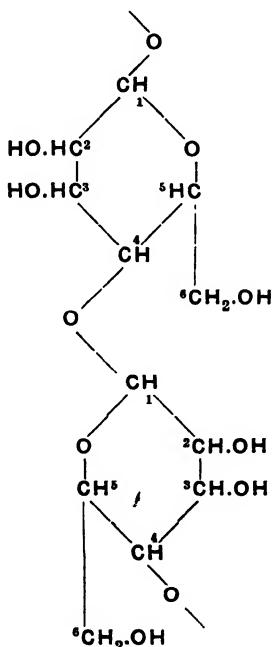
All varieties of cellulose have the percentage composition represented by the empirical formula  $C_6H_{10}O_5$ . The molecular formula is uncertain, but is some multiple of the empirical formula, and is written  $(C_6H_{10}O_5)_n$ , where  $n$  is probably not less than 200.

**General Properties of Cellulose.**—Pure cellulose is a white substance retaining the cellular structure of the material from which it is prepared. The specific gravity is 1.5. It burns freely in air with a luminous, smokeless

flame. When subjected to dry distillation it yields a mixture of volatile bodies, including acetic acid. It is hygroscopic, and forms a hydrate of the composition  $(C_6H_{10}O_5)_2 \cdot H_2O$ . Cellulose is insoluble in water and organic solvents, but dissolves in cuprammonium solution and concentrated solutions of certain salts, such as zinc chloride and calcium thiocyanate. It is insoluble in solutions of alkalis, but dissolves in cold concentrated sulphuric acid. Like other carbohydrates, when heated with concentrated sulphuric acid it swells up, forming a mass of carbon. It is attacked also by hydrochloric acid and by nitric acid. Cellulose is a colloid, and its solutions in cuprammonium and other solvents have the properties of typical colloidal solutions.

**Constitution of Cellulose.**—The constitution of cellulose is still uncertain. It is a complex alcohol containing both primary and secondary alcoholic groups. Like other alcohols, it yields, when oxidized, compounds containing aldehyde or ketone groups, which are oxidized further to carboxyl groups. Like alcohols, too, it can be esterified, and the esters, such as cellulose acetate, have important commercial applications. When treated with concentrated sodium hydroxide solution, it yields alkali cellulose,  $(C_6H_{10}O_5)_2 \cdot 2NaOH$ , which reacts as though it were  $C_6H_9O_4 \cdot ONa$ .

The structure of the cellulose micelles has been investigated by means of X-ray analysis. This indicates that they consist of chains of glucose residues linked together by oxygen atoms in the manner shown in the accompanying graphic formula:—



Two very important derivatives of cellulose are hydrocellulose and oxycellulose, owing to the fact that they are responsible for what is known as *tenderness* in cotton goods.

**Hydrocellulose.**—When cellulose is boiled with an aqueous solution of sulphuric or hydrochloric acid, it is hydrolysed gradually with the formation of dextrose,  $C_6H_{12}O_6$ . This change takes place in stages, the first product

of the hydrolysis being hydrocellulose. The rate of hydrolysis depends upon the hydrogen-ion concentration of the acid used and the temperature of the reaction. At 100° C. the rate of change is very rapid, and it is still more rapid at higher temperatures. It is not necessary to heat the cotton with the acid, prolonged contact at atmospheric temperatures being sufficient; whilst even 0.01 per cent. of either sulphuric or hydrochloric acid if allowed to dry into cotton will change it gradually into hydrocellulose, the production of which always causes "tenderness."

Hydrocellulose may be prepared by soaking purified cotton in a 2 to 3 per cent. solution of hydrochloric acid, squeezing out the excess liquid, drying by exposure to air, and then heating for four hours in a closed vessel at 70° C. The product retains the structure of the cotton, but is easily reduced to a powder by rubbing.

Hydrocellulose is more readily soluble in cuprammonium solution than is ordinary cellulose, and has an altered affinity for dyestuffs. It is said to reduce Fehling's solution, but this is due probably to adsorbed dextrose.

**Oxycellulose.**—Since cellulose is an alcohol containing both  $-\text{CH}_2\text{OH}$  and  $>\text{CHOH}$  groups, it is affected by oxidizing agents. The product of oxidation contains  $-\text{CQOH}$  and  $>\text{CO}$  groups, and is termed *oxycellulose*. Such oxidizing agents as bleaching-powder, nitric acid, permanganates, or air in the presence of an oxygen-carrier bring about this change. The bleaching of cotton is an oxidation process. When bleaching-powder is used, the colouring-matters are first oxidized, and protect the cellulose when the process is controlled. If, however, too much bleaching-powder is used, or unsuitable conditions obtain, the oxidation proceeds further, and oxycellulose is produced. The cotton is then said to be *over-bleached*. Both acid and alkaline oxidizing agents act in the same way, although giving different types of oxycellulose. In all cases the change is facilitated by the presence of an oxygen-carrier.

Oxycellulose may be prepared by the method of E. Knecht (*J. Soc. Dyers Col.*, 1920, **36**, 251). Thirty grams of filter-paper is pulped in 600 ml. of caustic soda solution of sp. gr. 1.5° Tw. The pulp is thinned with water, mixed with a slight excess of sulphuric acid, filtered, and washed with water. The washed residue is suspended in 600 to 900 ml. of dilute sulphuric acid (10° Tw.), and mixed thoroughly. A solution of 12 g. of potassium permanganate in dilute sulphuric acid (10° Tw.) is then added slowly, with constant stirring, during a period of two hours. After standing for two hours, the brown precipitate of oxycellulose and oxides of manganese is filtered off, washed, and treated with hydrogen peroxide and dilute sulphuric acid to reduce and dissolve the oxides of manganese. The oxycellulose is then filtered off, washed with water, and dried at a low temperature.

**Properties of Oxycellulose.**—Oxycellulose is a white amorphous substance, which when exposed to air becomes gradually yellow or brown. If present in bleached cotton it not only causes tenderness but also loss of colour. The change in colour is rapid at a temperature of 130° C. Owing to the presence of acid groups, oxycellulose has a marked affinity for basic dyestuffs such as methylene blue and safranin; if the acid groups predominate the product may be distinctly soluble in sodium hydroxide solution. The presence of carbonyl groups is indicated by the fact that oxycellulose gives a phenylhydrazone with phenylhydrazine, reduces Fehling's solution, and reacts with Schiff's reagent.

In the early stages of the oxidation of cotton, carbonyl groups are first formed. As the oxidation proceeds these are oxidized gradually to carboxyl groups, but more carbonyl groups are produced, that is, the latter predominate.

In the later stages of oxidation, when more of the alcoholic groups have been oxidized, the carboxyl groups predominate. There are, in fact, two distinct types of oxycellulose, the production of which depends chiefly upon the conditions which obtain. When oxidation takes place on the alkaline side of pH 7, carboxyl groups will predominate, whilst on the acid side of pH 7 the carbonyl groups will outnumber the carboxyl groups. The first type of oxycellulose has a low reducing power towards Fehling's solution, a marked affinity for methylene blue and distinct solubility in sodium hydroxide solution. The second type has a high reducing power, a small affinity for methylene blue, and slight solubility in sodium hydroxide solution. Both types lower the viscosity of a solution of cotton in cuprammonium solution.

These facts are of importance in the examination of bleached cotton. When a well-bleached sample is boiled with Fehling's solution under specified conditions, and the precipitated cuprous oxide determined, the equivalent of copper should not exceed 0.2 g. per 100 g. of cotton. This is termed the *copper value*. If the sample is treated with a cold aqueous solution of methylene blue, the quantity absorbed should not be more than 0.5 to 0.6 millimols per 100 g. of cotton. This figure is the *methylene-blue number*. When either oxycellulose or hydrocellulose is present in cotton, the viscosity of a solution of the sample in cuprammonium solution is found to be lower than that of undamaged cotton, and the extent of the damage can be inferred from the fall in viscosity. This is known as the *fluidity number*. Full details of these tests are given in the present authors' *Textile Analysis* (Griffin & Co.).

*Qualitative Tests for Oxycellulose.*—The methylene-blue and copper-reduction tests may be used qualitatively. If a sample of cotton is stained deeply by a cold aqueous solution of methylene blue, or becomes red when boiled with Fehling's solution, it is almost certain that oxycellulose is present. Other special tests are—

(1) *Phenylhydrazine test*. The cotton is soaked in a solution of phenylhydrazine in acetic acid. Oxycellulose gives a yellow hydrazone.

(2) *Ditz's test*. Cotton containing oxycellulose (or hydrocellulose) when soaked in Nessler's solution becomes at first dark brown and then pale or dark grey, owing to reduction of the mercuric salt.

(3) *Knapp's test*. The sample is dyed in a boiling solution of benzo-purpurine. It is then rinsed with water, placed in a beaker, and treated carefully with dilute hydrochloric acid until the colour changes to blue. It is next rinsed with hard water to neutralize the acid. The red colour reappears on the cotton, but oxycellulose remains dark blue.

(4) *Freiberger's test*. The material is soaked in a solution of sodium ricinoleate, squeezed, and steamed. In the presence of oxycellulose a yellow colour is produced.

*Cellulose Peroxide.*—It was found by C. F. Cross and E. J. Bevan that when cotton is acted upon by ozone and other powerful oxidizing agents, such as potassium persulphate, in the presence of sulphuric acid, a body is formed which has the properties of a peroxide, liberating iodine from potassium iodide like other peroxides. They termed this compound *cellulose peroxide*.

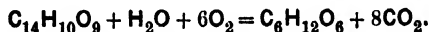
### Tannic Acid.

Tannic acid,  $C_{14}H_{10}O_8$ , is commonly present in vegetable tissues, and cotton may contain it in small quantities. It exists generally in the form of a *glucoside*, which is a substance giving glucose as one product when hydrolysed

by an acid or an enzyme. Glucosides are very common in vegetable tissues. The following are a few important examples:—

- (1) Tannin . . .  $C_{34}H_{26}O_{22} + 2H_2O = 2C_{14}H_{10}O_9 + C_6H_{12}O_6$ .
- (2) Indican . . .  $C_{14}H_{17}O_6N + H_2O = C_8H_7ON + C_6H_{12}O_6$ .  
Indoxyl
- (3) Madder . . .  $C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6$ .  
(Ruberythric acid) Alizarine
- (4) Amygdalin . . .  $C_{20}H_{27}O_{11}N + 2H_2O = C_6H_5CHO + HCN + 2C_6H_{12}O_6$ .  
Benzaldehyde

Tannic acid is made by extracting gall-nuts with water. When pure it is a colourless crystalline substance which is readily soluble in water. It is a weak acid and forms salts with metals. The tannates of the heavy metals are insoluble in water. Ferric tannate, which is bluish-black in colour, sometimes causes discolorations in cotton goods. When an aqueous solution of tannic acid is boiled, it is changed gradually into gallic acid,  $C_6H_2(OH)_3.COOH$ . All varieties of tannic acid give an insoluble precipitate with a solution of gelatin or a soluble protein. When their aqueous solutions are exposed to air, oxygen is absorbed, with the production of a brown colour. Unripe cotton contains a distinct quantity of tannic acid, which mostly disappears as ripening proceeds, probably owing to oxidation in accordance with the equation:



Tannic acid is used in the mordanting of cotton and in the weighting of silk.



## CHAPTER X.

### SPECIAL PROPERTIES OF COTTON CELLULOSE.

**Action of Heat.**—Cotton may be heated in the dry state to a temperature of 150° C. without undergoing decomposition, but if the heating is prolonged it becomes gradually brown. At higher temperatures this change takes place more rapidly. The same result is produced by heating it at a lower temperature for a longer period. The browning is due to the gradual formation of oxycellulose, which also produces tendering.

Moist heat is not so destructive in its action, but if cotton is heated for a long time with steam it is slowly changed into hydrocellulose.

**Action of Air.**—Prolonged exposure to air, especially in the presence of sunlight, has an effect upon cotton somewhat similar to that of dry heat, gradually producing oxycellulose, accompanied by loss of tensile strength. In considering the action of air, several factors must be taken into account, *viz.* the action of (i) light, (ii) moisture, (iii) oxygen and traces of ozone or hydrogen peroxide, and (iv) micro-organisms.

The action of light is due chiefly to the ultra-violet rays. The effect of these has been studied by Dorée and Dyer (*J. Soc. Chem. Ind.*, 1917, **36**, 211). They found that when a scoured and bleached cotton fabric was exposed continuously for a week at a temperature of 30° to 35° C. to the light from a Cooper-Hewitt mercury-vapour lamp, placed about one foot above the fabric, a distinct change was noticeable. The upper surface of the fabric became biscuit-yellow in colour, and lost tensile strength. Oxycellulose could also be detected on the material. The strength in the affected parts of the fabric had entirely gone; the appearance of transverse cracks with occasional swollen places, similar to the effects produced by the excessive action of alkali, was noted. The affected parts were much more absorbent and wetted out more readily than the unaffected parts of the fabric. These workers concluded that ultra-violet rays, in the presence of air and moisture, probably act in two ways: (i) by a specific physical action causing disintegration of the cellulose, and (ii) by the development of ozone, which oxidizes the cellulose to a peroxide. Dorée and Cunningham had already observed that air containing from 1 to 2 per cent. of ozone attacks cotton rapidly, forming a substance termed by them *cellulose peroxide* (see p. 108), together with an acid and carbon dioxide. The tensile strength of fabrics exposed to the action of ozonized air decreased also very rapidly, falling, in the case of an Egyptian yarn, from 100 to 53 in twelve hours. Turner (*J. Soc. Dyers Col.*, 1920, **36**, 165) also studied the effect of light. He found that the presence or absence of moisture did not affect the results, but that removal of oxygen from the surrounding atmosphere very largely reduced, yet did not entirely inhibit, the destructive effect of light. He supports the view that the ultra-violet rays have a definite specific action

on cellulose, but that in the presence of oxygen the effect is greater and of a chemical character, probably due to the formation of ozone. The action of light in the presence of air is accelerated greatly by the presence of traces of metals, such as copper, which act as oxygen-carriers. Cotton frequently contains traces of copper derived from machines used in spinning or weaving. The authors have examined cotton shirts which, after being worn for three months exposed to a tropical sun, became quite tender, particularly in those parts, such as the shoulders, which received most of the light. Analysis showed that the damaged portions consisted largely of oxycellulose and that traces of copper were present. The latter had undoubtedly played an important part in the destruction of the fabric.

**Action of Water.**—Cold water causes cotton to swell, but has no chemical action on it, though, of course, any water-soluble impurities which may be present are dissolved. The swelling is accompanied by the disappearance of the natural twist, which reappears on drying. When cotton is boiled with water a slight shrinkage takes place, reaching, in the case of yarn, a maximum of about 2 per cent. with prolonged boiling. The shrinkage is accompanied by a small decrease in tensile strength.

Sea water is sometimes the cause of damage to cotton fabrics. C. Dorée (*Biochem. J.*, 1920, 709) found that exposure to the action of sea water for from three to five weeks made both cotton and linen fabrics quite tender. This change was accompanied also by a great alteration in chemical properties, no less than 17 per cent. of the cotton having become soluble in boiling 1 per cent. sodium hydroxide solution. The variable factors involved in the action of sea water on cellulose are oxygen, light, and bacteria or moulds. Dorée conducted experiments to determine the effect of these factors, and concluded that micro-organisms in the presence of oxygen were the active cause of destruction.

**Action of Micro-organisms.**—It has been mentioned above that the destructive effect of the prolonged action of sea water on cotton is due to the growth of micro-organisms. Bacteria and moulds are often responsible for damage in cotton goods. It is well known that cotton deteriorates when exposed to the action of a damp atmosphere. Fleming and Thaysen (*Researches on Cellulose*, 4, 219) have established the following points: Moisture in itself has no deleterious action. The damage is caused by micro-organisms always present in raw cotton, and these do not attack the fibre unless over 9 per cent. of moisture is present. Thus, good Indian cotton, which contained normally 1.4 million bacteria per gram, showed no increase on this number when kept for three days at 16° C. in the presence of 6, 7, 8, and 9 per cent. of water. With 10, 15, 20, and 50 per cent. of water respectively the numbers increased to 124, 499, 1112, and 9040 millions. Fibres which have been damaged by bacteria may be detected by means of the *swelling test*. From 0.1 to 0.3 g. of the cotton is boiled in a 1 per cent. solution of sodium hydroxide, soured in acetic acid, washed, and steeped in 1.5 ml. of 15 per cent. sodium hydroxide, followed by the addition of 1.5 ml. of carbon disulphide. After fifteen to forty-five minutes some of the fibres are placed on a microscope slide and covered with a glass slip, and a drop of water is allowed to diffuse underneath. When magnified some 50 diameters a normal fibre shows characteristic swellings like those given by Schweitzer's solution (see Fig. 53). A fibre which has been attacked by bacteria gives quite different results. The cuticle and most of the cellulose have been perforated in many places, and the former has lost its power of resistance, so that the latter swells regularly, no globular formations being seen. By counting the proportion of such fibres an

estimate of the amount of damage may be formed. Schweitzer's solution also is suitable for this swelling test.

The present authors (*J. Soc. Chem. Ind.*, 1924, 43, 190 r) made some experiments with *Bacillus subtilis* and Egyptian cotton. They found that, first of all, the fibres imbibed water and lost their characteristic twist, thus being changed into swollen tubes. In the earlier stages of the action, probably before the perforation of the cuticle mentioned above, swellings were occasionally seen. Occasionally a fibre was seen in which the swollen cell-walls had ruptured the cuticle (Figs. 58 and 59). The swelling of the cell-walls was accompanied by an increase in tensile strength from 15.4 to 18.5 oz. in five days. After this the cuticle was destroyed, and the tensile strength decreased to a figure below that of the original cotton.

After a time the globular swellings disappeared, and the fibres became uniformly swollen and devoid of twist. When treated with Schweitzer's solution they swelled up uniformly, showing that the cuticle had been attacked



Fig. 58.—Cotton Fibre attacked by *B. subtilis*.



Fig. 59.—Cotton Fibres ruptured.

or destroyed. Prolonged action of many bacteria and moulds causes the complete disintegration of the fibre.

Fleming and Thaysen (*loc. cit.*) found that American was less susceptible than Indian cotton to bacterial attack. Egyptian is intermediate in this respect between American and Indian cottons. Cotton grown in India from American seed appears to be as resistant as American cotton.

The decomposition of cellulose in Nature by micro-organisms is a matter of considerable importance. This has been studied by Groenewege (*J. Soc. Chem. Ind.*, 1921, 40, 76A), who concluded that the process is a symbiotic one. He isolated three varieties of *Bacillus cella-resolvans*, which attacked cellulose, reducing it to a pulp and producing acetic, butyric, and lactic acids. The products resulting from this process serve as food for denitrifying organisms such as *Bacillus opalescens* and *Bacillus viscosus*, which, as they grow, complete the dissolution of the disintegrated cellulose produced by *Bacillus cella-resolvans*, oxidizing the acetic, butyric, and lactic acids to carbon dioxide and water. He thinks it probable that enzymes such as cellulase are secreted, which are concerned in the action.

The action of acids on cellulose was referred to in the last chapter. They act upon cotton in a similar manner, producing either hydrocellulose or oxy-

cellulose according to the conditions, or entirely changing it into simpler compounds such as dextrose. But under certain conditions an effect similar to mercerization is produced by strong mineral acids.

**Action of Sulphuric Acid.**—Cold concentrated sulphuric acid dissolves cotton rapidly, forming at first a solution of hydrated cellulose,  $(C_6H_{10}O_5)_2 \cdot H_2O$ . If this solution be kept for any time, the hydrated cellulose becomes hydrolysed to dextrose. When the solution is warmed the cellulose is decomposed rapidly, carbon being formed and sulphur dioxide evolved. Prolonged heating with concentrated acid causes the complete oxidation of the cellulose into carbon dioxide and water. If the solution of cellulose in sulphuric acid be poured, at once, into an excess of cold water, the hydrated cellulose is thrown down as a gelatinous precipitate termed *amyloid*. This reaction is used in the manufacture of vegetable parchment. Sheets of paper are immersed for a short time in concentrated sulphuric acid, and then washed rapidly in cold water till free from acid. In this way the pores of the paper become filled up with impervious hydrated cellulose, which gives the paper properties similar to those of parchment. Cold solutions of sulphuric acid of moderate concentration, if allowed to act on cotton for a short time and then washed out rapidly, produce an effect similar to that of mercerization—that is, the cotton shrinks, has an increased tensile strength, and a greater affinity for direct dyestuffs. This effect is produced by solutions containing 62 per cent. of acid, or of 105° Tw. density. Cold dilute solutions of sulphuric acid have no action on cotton, and if subsequently washed out completely no diminution of tensile strength nor any hydrocellulose can be detected. But if the acid is allowed to dry in, or if the cotton is boiled with it, the effect is very different. When cotton is boiled with dilute solutions of sulphuric acid it is tendered rapidly, and this tendering becomes apparent as diminished tensile strength, even before any hydrocellulose can be detected. Prolonged boiling, with even traces of acid, will transform the cotton completely into hydrocellulose. This action is of importance in dyeing cotton in acid dye-baths.

When dilute solutions of sulphuric acid are allowed to dry into cotton, the tendering action is very marked. One part in 10,000 is sufficient to cause gradual tendering, the action being much more rapid if the cotton is warmed or ironed. Traces of sulphuric acid are a common cause of tenderness in cotton goods. It should be remembered that the acid acts only as a hydrolysing agent, and that, theoretically, even traces can change an indefinite quantity of cotton into hydrocellulose. Lawrence (*J. Soc. Chem. Ind.*, 1919, 38, 894A) found that the action depended on (i) the concentration of the acid, and (ii) the temperature of drying. For example, while 0.01N. sulphuric acid dried into cotton at 20° C. caused a loss of tensile strength of 2 per cent., 0.2N. acid at the same temperature reduced it by 67 per cent.

Knecht and Thompson (*J. Soc. Dyers Col.*, 1921, 37, 270) concluded that when dilute sulphuric acid is dried into cotton the action is of two kinds. The cellulose is partly hydrolysed, which accounts for the tendering observed, and some sulphuric acid is also fixed, which acts as a mordant for basic dyes. But the increased affinity for basic dyes does not depend on the degree of tendering. Thus, if cotton is simply boiled with the acid without allowing it to dry in, although the tensile strength is diminished, its affinity for methylene blue is, if anything, slightly decreased. Nor is any sulphuric acid fixed in the fibre. Thus, cotton which shows tenderness without an increased affinity for basic dyes owes its tenderness probably to prolonged exposure to weak, hot sulphuric acid which has not been allowed to dry in, i.e. it is due to hydrocellulose produced by hydrolysis only. But if the acid is allowed to dry,

hydrolysis is accompanied also by oxidation to some form of oxycellulose. This results not only in increased tenderness, but also in a greater affinity for methylene blue or its leuco compound. Both unoxidized and oxidized sulphuric-acid-treated cotton resist dyeing with Diamine Sky-blue, but if both are boiled with a 5 per cent. solution of sodium hydroxide for half an hour and then washed, the affinity is restored in the case of the oxidized, but not of the unoxidized, cotton.

**Action of Hydrochloric Acid.**—Ordinary cold concentrated hydrochloric acid does not dissolve cotton, but is said to have a mercerizing action like that of sulphuric acid of 105° Tw.; but a solution containing 40 per cent. of hydrochloric acid, corresponding to a specific gravity of 1.209, is able to dissolve it. The relative effects of hydrochloric and sulphuric acids in tendering cotton are illustrated by the following experiments of Fort and Pickles (*J. Soc. Dyers Col.*, 1915, 31, 255), who boiled cotton with different acids of the same concentration, and then determined the loss in tensile strength. As an example, they found that with normal acid the percentage losses were 93.5 for hydrochloric, and 71.0 for sulphuric, acid.

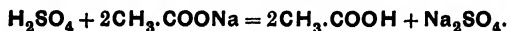
Thompson (*J. Soc. Dyers Col.*, 1915, 31, 255) obtained similar results. He found that 0.0025 per cent. of hydrochloric acid when dried into cotton caused as much tenderness as 0.0078 per cent. of sulphuric acid. When cotton was boiled with the acid, 0.0078 per cent. of hydrochloric acid was equivalent in tendering effect to 0.03125 per cent. of sulphuric acid.

**Inhibition of the Tendering Effects of Acids.**—The only way to inhibit entirely the tendering action of strong acids is to remove them completely by washing with water or dilute solutions of mild alkalis. But the effect can be partly inhibited by

(1) The presence of a sodium salt of the same acid.

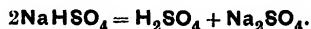
(2) Adding a salt of a weaker acid.

If sodium sulphate be added to a solution of sulphuric acid, it tends to retard the dissociation of the acid into its ions and, therefore, to reduce the hydrogen-ion concentration. Thus, it practically converts the strong into a weaker acid with, naturally, a smaller tendering action. The addition of a salt of a weaker acid causes the stronger acid to be replaced by the weaker. Thus with sulphuric acid and sodium acetate:



But it must be remembered that this reaction is reversible under certain conditions. Excess of sodium sulphate, for example, would tend to reverse the action, causing the liberation of sulphuric acid.

**Acid salts** of the mineral acids act just like the acids, except that their hydrogen-ion concentration is lower. Sodium acid sulphate, dissolved in water, acts as though it were a mixture of sulphuric acid and sodium sulphate:



Any salt whose aqueous solution is acid to litmus-paper also has a tendering action. This is, of course, due to the free acid liberated by hydrolysis. The action is particularly marked in the case of such salts as magnesium and aluminium chloride, which are still more hydrolysed on drying.

**Action of Salts.**—Many salts in aqueous solution act on cellulose, either as swelling agents or as solvents according to the concentration of the solution. Zinc chloride, calcium thiocyanate, and calcium chloride are examples.

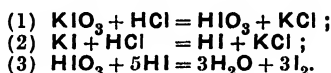
**Action of Nitric Acid.**—Owing to its oxidizing properties, the action of nitric

acid on cotton is not quite the same as that of hydrochloric and sulphuric acids.

Cold concentrated nitric acid of from 76° to 83° Tw. strength has a mercurizing action, causing shrinkage, increased tensile strength, and affinity for dyestuffs. If the acid is washed out under tension to prevent shrinkage, an increased lustre similar to that of mercerized cotton is also produced. Certain patent processes for the purpose of producing "wool-like" effects on cotton depend upon this action of nitric acid. With acid of below 76° Tw. no mercerizing action is observed, but the cotton is oxidized gradually to oxycellulose, and ultimately to simpler compounds, such as oxalic acid. The reaction is hastened by boiling. Cold dilute nitric acid has little action on cotton, but if allowed to dry in, a mixture of hydrocellulose and oxycellulose is produced. When cotton is treated with a mixture of cold concentrated sulphuric and nitric acids, bodies termed *cellulose nitrates* are formed. The most important of these are the tri- and tetranitrates,  $C_{12}H_{17}(ONO_2)_3O_7$ , and  $C_{12}H_{15}(ONO_2)_4O_8$ . They are used in the manufacture of collodion, celluloid, and rayons. Guncotton is cellulose hexanitrate,  $C_{12}H_{14}(ONO_2)_6O_4$ .

**Detection of Traces of Mineral Acid.**—Traces of free mineral acid may sometimes be detected by moistening the sample with hot distilled water, and then wrapping it round a piece of blue litmus-paper or paper stained with methyl orange. If pressure be applied, the colour change may be observed. Occasionally so much acid is present that it can be detected by merely soaking the fabric in distilled water and testing with litmus or methyl orange. But the most delicate indicator is methyl red, which is able to detect as little as 0.005 per cent. of acid. It is yellow in the presence of traces of alkali, and red with 0.005 per cent. of acid and upwards.

Briggs (*J. Soc. Chem. Ind.*, 1916, 35, 81) recommends the use of a solution of potassium iodate, potassium iodide, and starch as an indicator. In the presence of mineral acid, free iodine is liberated, which colours the starch blue. The reactions are



The solution is made up with distilled water and a little boiled starch. A drop or two of decinormal hydrochloric acid is added till the liquid just shows a faint blue colour. This is to ensure neutrality. The mixture is then boiled till the colour is discharged, and cooled. If a fabric be treated with this reagent, a blue colour appears if mineral acid is present, the time required for it to develop depending on the amount of acid present. If no sign of a blue stain is visible after five minutes the material may be regarded as safe.

**Action of Organic Acids.**—Organic acids do not attack cotton nearly so readily as the mineral acids, owing to their lower hydrogen-ion concentration and the fact that in some cases they are volatile. But oxalic acid, which is not volatile and has also a rather high hydrogen-ion concentration, does cause tendering. If cotton is boiled with solutions of organic acids it is gradually tendered. In dyeing mixtures of wool and cotton with acid dyes, formic or acetic acid is generally substituted for sulphuric in order to limit the tendering effect as much as possible. It is, however, impossible to eliminate it entirely. Zanker and Mann (*J. Soc. Chem. Ind.*, 1917, 36, 708) found that when cotton is boiled with acetic or formic acid, under exactly the same conditions as those of an acid bath, the loss of strength was from 40 to 45 per cent. in the case of acetic, and from 50 to 55 per cent. with formic, acid. Formic acid has a greater hydrogen-ion concentration than acetic acid. The

addition of sodium sulphate decreased the tendering action, but in the presence of wool (*i.e.* in unions) it increased the loss of tensile strength to 50 and 60 per cent. respectively. This is due probably to the fact that wool adsorbs the basic ions of the sodium sulphate and sets free the acid ions, thus increasing the hydrogen-ion concentration of the bath. The tendering of cotton in the dyeing of unions is a matter of great importance.

**Action of Alkalis.**—While acids tender cotton, alkalis, except under certain conditions, do not. Mild alkalis, such as sodium carbonate or borax, have no action on cotton in the absence of air, either at low or at high temperatures. In the presence of oxygen, however, oxycellulose is gradually produced, and, consequently, tendering occurs. Dilute solutions of strong alkalis act in the same way. In the complete absence of air, cotton may be boiled, under pressure, with a 2 per cent. solution of sodium hydroxide without the least tendering. But if oxygen is present, it is attacked rapidly. This may be shown experimentally by boiling some cotton yarn in a 2 per cent. solution of sodium hydroxide to which a little manganese chloride has been added as an oxygen-carrier. If a stream of air is drawn through the boiling liquor the cotton rapidly becomes too tender to handle.

If cotton has been boiled with sodium hydroxide it is very difficult to wash out all the alkali with water. This is due to the fact that cellulose adsorbs sodium hydroxide, forming the unstable compound termed *alkali cellulose*,  $C_{12}H_{20}O_{10} \cdot 2NaOH$  (or  $C_6H_{10}O_5 \cdot NaOH$ ). This was observed first by Mercer, who stated that a definite chemical compound of the formula  $(C_6H_{10}O_5)_2 \cdot 2NaOH$  is formed, which when the cotton is washed gives up the sodium hydroxide; becoming changed into cellulose hydrate,  $(C_6H_{10}O_5)_2 \cdot H_2O$ . The discovery of Mercer's was of great importance, because he observed that, after washing, the cotton had acquired new properties. These were

- (1) It had decreased in length;
- (2) Its tensile strength was increased;
- (3) It had an increased affinity for dyestuffs.

This was the starting-point of the process of *mercerization*. But, unfortunately, the increased tensile strength and affinity for dyestuffs did not compensate manufacturers or dyers for the extra trouble involved and the loss of length. The process was not commercially successful till Lowe, some years later, in 1889, discovered that if the cotton were prevented from shrinking, the treated cotton not only retained the increased tensile strength and affinity for dyestuffs, but acquired new properties still more valuable, namely:

- (1) A greatly increased lustre;
- (2) A soft, silky feel;
- (3) An increased power of responding to mechanical finishing processes, such as schreinerizing.

Lowe's work, which was patented, laid the foundations of a successful commercial process; but still it was not till some years afterwards, in 1895, that the method became at all extensively used. Quite apart from the commercial value of Mercer's work, it was of much scientific importance, and led many other chemists to investigate the subject. The first of these was Gladstone, who found that by washing Mercer's alkali cellulose with alcohol, part of the alkali could be removed, leaving a residue having the composition expressed by the formula  $(C_6H_{10}O_5)_2 \cdot NaOH$ , which Gladstone thought to be a definite chemical compound termed by him "alkali cellulose." This, on further washing with water, he found to be resolved into cellulose hydrate,  $(C_6H_{10}O_5)_2 \cdot H_2O$ . Hübner and Pope (*J. Soc. Chem. Ind.*, 1904, 23, 404) concluded, from measurements of shrinkage and affinity for dyestuffs, that cotton

yarns adsorb sodium hydroxide in amounts which increase rapidly as the strength of the sodium hydroxide solution increases from 20° to 26° Tw. The adsorption increases more slowly between 26° and 30° Tw., and reaches a maximum at 45° Tw. These experiments seemed to indicate the formation of definite compounds of cellulose with the alkali. Vieweg arrived at somewhat similar conclusions, but by chemical methods. He used solutions of sodium hydroxide of accurately determined strength. After soaking the cotton in these for a sufficient time to allow of complete adsorption, he again determined the strength of the solution. From the difference in concentration of the original and final solutions, he calculated the amount of sodium hydroxide adsorbed by the cotton. Vieweg concluded that the maximum adsorption corresponds to the formula  $C_{12}H_{20}O_{10} \cdot 2NaOH$ . The curve expressing the percentage of alkali taken up shows two horizontal portions where there is no further increase in the quantity adsorbed. The first of these begins at a concentration of 16 g. of sodium hydroxide per 100 ml. and ends at 24 g. The second horizontal portion begins at 35 g. per 100 ml. and remains horizontal, i.e. further increase in the concentration does not cause any more adsorption. These two horizontal portions correspond to the formulæ  $(C_6H_{10}O_5)_2 \cdot NaOH$  and  $(C_6H_{10}O_5)_2 \cdot 2NaOH$  respectively, and indicate again the formation of definite compounds. But other chemists reached different conclusions, and it is now generally held that, although cotton or cellulose does adsorb alkali, there is no definite compound produced. Thus Leighton (*J. Soc. Chem. Ind.*, 1916, 35, 249), after reviewing the work of former experimenters, states that "there is no experimental evidence for the formation of any compound of cotton with sodium hydroxide." Whether or not alkali cellulose is a chemical compound, it is certain that in many cases it reacts as though it had the constitution  $C_6H_7O_4 \cdot ONa$ . The manufacture of viscose is an example. Further details of the action of sodium hydroxide on cotton may be found in S. R. Trotman and E. L. Thorp's *Principles of the Finishing and Bleaching of Cotton* (Griffin & Co.).

**Mercerization of Cotton.**—The process itself is comparatively simple. The cotton must, first of all, be thoroughly scoured to render it permeable. It is then soaked in a cold solution of sodium hydroxide for a short time, and washed thoroughly with water.

It is immaterial whether the cotton is prevented from shrinking throughout the operation, or stretched to its original length while being washed. Thus the goods may be stretched on frames from the beginning, or impregnated with the lye by means of a mangle, and then stretched and washed. The former method is adopted for yarns, and the latter is more convenient for piece-goods. The following are examples of the methods used: In the case of cotton yarns the hanks are scoured by boiling with a solution of sodium carbonate and soap, washed, and hydro-extracted. They are then soaked, under tension, in a cold solution of sodium hydroxide of from 55° to 65° Tw. strength (or specific gravity 1.300). The action is very rapid, ten minutes being sufficient if the goods are well scoured and permeable. The temperature must not exceed 65° F. (18.3° C.). The goods are then squeezed, and rinsed with cold water, still under tension, till nearly free from alkali. They are then soaked in a bath containing a little acetic acid to neutralize the last traces of alkali, after which they are again thoroughly washed with water, and dried. Before drying, the goods may be soaped to improve the lustre, and if a scroop is required they are finally soaked in a 0.5 per cent. solution of acetic or tartaric acid, squeezed, and dried. When mercerizing yarns, only longitudinal tension is necessary, but pieces require both longitudinal and lateral extension. They



may be impregnated with the lye by means of a mangle. As the cotton leaves the mangle it is seized by a moving clip stenter and stretched to its greatest possible width. Halfway down the frame it meets a sprinkler, which commences the washing process. This is followed by two or three more sprinklers whilst the cloth is still in the clips. The washing is done on the counter-current principle—that is, pure water meeting the cloth from the sprinkler at the far end of the stenter. The washings from this are pumped to the next sprinkler, and from this to the next, so that each sprinkler treats the cloth with a more concentrated solution of lye. Thus, the washings from the sprinkler nearest the impregnating mangle are the most concentrated. They are recausticized with lime, concentrated, and used again.

Fig. 60 illustrates a mercerizing machine made by Sir James Farmer, Norton, and Company. It consists of an impregnating mangle, stenter with a cascade washing arrangement above the cloth, and suction boxes underneath. It has also a special steaming chamber and washing-off tanks.

Mercerization may be applied also for the production of purely local effects, or fabrics may be soaked in solutions of sodium hydroxide merely in order to shrink them and increase their tensile strength. In the latter case no tension is used. The mercerizing effect of solutions of caustic soda is connected with their temperature and concentration. With dilute solutions a better lustre is obtained at low than at higher temperatures; and a solution which is below mercerizing strength at ordinary temperatures can be made effective by refrigeration. Most observers hold that the lustre produced at low is greater than that at high temperatures, but Knecht and Harrison (*J. Soc. Dyers Col.*, 1923, **39**, 311) found that, although a 25 per cent. solution of caustic soda produced a better lustre at 10° C. than at 80° C., with a 43 per cent. solution the results were the opposite. But others maintain that there is little difference in lustre caused by temperature, while a higher temperature assists penetration of the lye. If cotton be previously treated with formaldehyde, it cannot be mercerized, nor dyed with direct dyestuffs.

**Properties of Mercerized Cotton.**—Mercerized cotton is more easily acted upon by chemical reagents than ordinary cellulose. When it is boiled with dilute acids it is hydrolysed slowly, and gives rise to bodies which reduce Fehling's solution. Similarly, it is more readily changed into oxycellulose, and dissolves more rapidly in Schweitzer's solution. When mercerized cotton is treated with this reagent no globular swellings can be observed. This is taken to indicate that the cuticle has been either altered or destroyed during the mercerizing process. Mercerized cotton absorbs more water than ordinary cotton when exposed to damp air, and this power increases with the concentration of the caustic soda used in mercerizing. The greater affinity for direct dyes also increases with the concentration of the mercerizing liquor. For fuller details of the properties of mercerized cotton the *Journal of the Society of Dyers and Colourists*, Oct. 1923, **39**, 303, should be consulted.

**Microscopic Structure of Mercerized Cotton.**—The process of mercerization is accompanied by an important change in the microscopic appearance of the fibre. This has been very fully described by Pope and Hübner (*J. Soc. Chem. Ind.*, 1904, **23**, 408). If cotton fibres are treated under a microscope with cold concentrated sodium hydroxide solution, they can be seen to swell, and then gradually untwist, till they appear like swollen tubes instead of twisted cells. If this experiment is carried out under tension, produced by fixing the ends of the fibre to the slide with wax, the untwisting of one portion of the fibres tends to cause the twisting of another portion, the torsion thus produced giving rise to a series of ridges on the surface of the untwisted fibre.

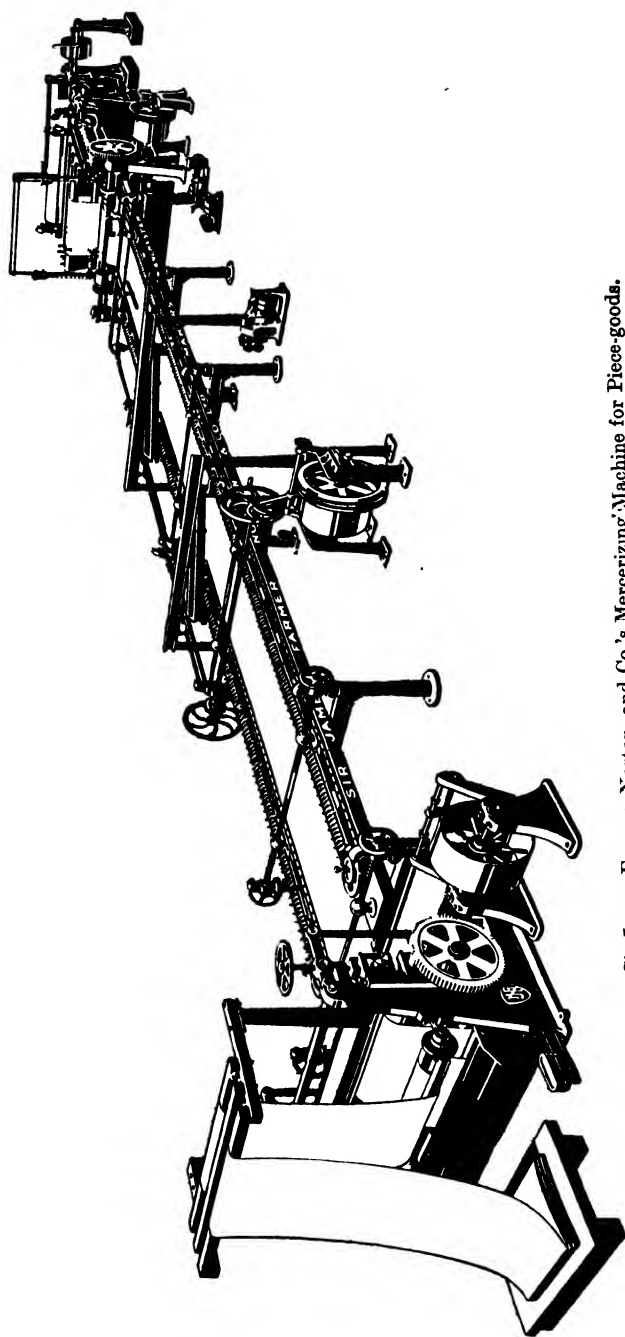


Fig. 60.—Sir James Farmer, Norton, and Co.'s Mercerizing Machine for Piece-goods.

These ridges are thought by Pope and Hübner to be the cause of the increased lustre. But other observers, including Harrison (*J. Soc. Chem. Ind.*, 1915, **34**, 1087), maintain that the "ridges" do not actually exist, and that the increased lustre is due to the smooth surface of the fibre reflecting the light which falls upon it. Fig. 61 shows the appearance of mercerized cotton under the microscope.

**Tests for Mercerized Cotton.**—Mercerized cotton is distinguished from ordinary cotton by its tubular appearance and absence of twist. The proportion of tubular fibres in a sample gives a measure of the degree of mercerization. There are also some useful colour reactions:

(1) *Lange's Test.*—The following solutions are required: (a) 5 g. of potassium iodide and 1 g. of iodine dissolved in 16 ml. of water; (b) 25 g. of zinc chloride in 12 ml. of water. These solutions are mixed and allowed to settle, after which the clear liquid is decanted off for use. A portion of the sample to be tested is soaked in the reagent for about three minutes. Both mercerized and unmercerized cotton will become brown. The sample is then washed with boiled and cooled distilled water until the brown colour due to excess of iodine has changed to dark blue-black. The sample is now placed in fresh water. Unmercerized cotton will lose its colour very quickly, while the bluish colour persists for a considerable time in mercerized cotton.



Fig. 61.—Mercerized Cotton.

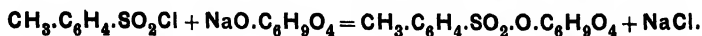
(2) *Knecht's Test.*—A sample is boiled for thirty minutes side by side with a similar sample of unmercerized cotton in a 0.5 per cent. solution of benzopurpurine. The samples are then washed and dried, after which the colours are compared. Mercerized cotton will be more deeply dyed than the unmercerized sample. By estimating the dyestuff on the fibre it is possible to obtain a measure of the degree of mercerization. Unmercerized cotton takes up 1.77 per cent. of benzopurpurine, while cotton mercerized with caustic soda solution of 65° Tw. absorbs 3.6 per cent.

(3) *David's Test.*—The material is spotted with strong sodium hydroxide solution, washed, and dyed with benzopurpurine. If unmercerized or incompletely mercerized, the spotted parts will dye more deeply than the rest of the sample.

**Schreinerized Cotton.**—The Schreiner process produces a lustre similar to that of mercerized cotton, but there is no alteration in microscopic structure nor increased affinity for iodine or dyestuffs. This process is used only for piece-goods. The pieces are run over a hot cylinder engraved with very fine lines whose direction turns obliquely to the length of the cloth. These lines are so fine and close together that they are invisible to the eye, but, owing to reflection of light by the embossed pattern they form, a greatly increased lustre is produced.

**Action of Dyestuffs.**—Cotton has no affinity for either acid or basic dyestuffs. It is sometimes dyed with basic dyes upon a tannic-acid mordant fixed by means of antimony. It is, however, generally dyed with the substantive and sulphur dyestuffs, for both of which it has a direct affinity. Indigo and vat dyes also are applicable to cotton, as well as such colours as aniline black and para red, which are actually produced upon the fibre.

**Immunized Cotton.**—When alkali cellulose is treated with a solution of *p*-toluenesulphochloride in toluene, the following reaction takes place:



The cellulose ester formed is comparatively stable, and resists dyeing with direct dyestuffs. Cotton treated in this way can be used for the production of thread effects. It is treated with an alcoholic solution of caustic soda, and the excess squeezed out. It is then heated with the *p*-toluenesulphochloride solution for an hour, washed, soaped, rinsed, and dried.

**Amidated cotton**, or amino cellulose, is made by heating immunized cotton with ammonia under pressure. The reaction which takes place is represented by the equation:



Amidated cotton has dyeing properties similar to those of wool.

## CHAPTER XI.

### MULTICELLULAR VEGETABLE FIBRES.

#### Flax.

ALL vegetable textile fibres, other than cotton, are multicellular—that is, composed of a number of cells cemented together. Moreover, they are not, unlike cotton, hairs attached to the seed, but part of the stem or some other tissue of the plant. In the case of flax they consist of what are termed *bast fibres* from the inner lining of the

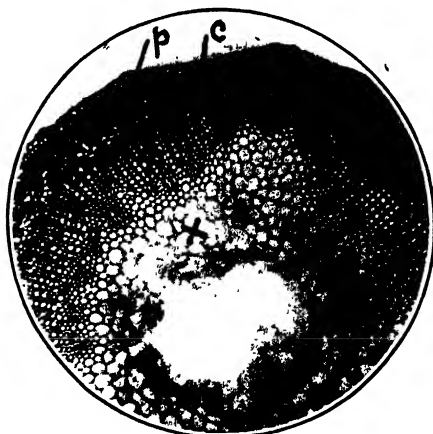


Fig. 62.—Stem of Flax.

fibres from the inner lining of the fibrous bark of a plant belonging to the natural order Linaceæ and species *Linum usitatissimum*. The flax plant is widely distributed, and is cultivated commercially in such countries as Russia, Belgium, Holland, England, and Ireland. Courtrai flax, the most valuable variety, is grown in Belgium. The plants, which are herbaceous, are grown each year from seed. When ripe, they are pulled out of the ground and allowed to wither. The stalks, leaves, and seed are then separated from one another by combing. The withered stalks contain about 75 per cent. of bast fibres. The seeds are crushed to press out

the linseed oil, and the residue, after pressing out this oil, is made into linseed cake, which is much used as a food for pigs and cattle. If a transverse section of the stem of the flax plant is examined under a microscope, it can be differentiated into the following parts (Fig. 62):

The outermost layer *c* is termed the *cuticle*. Beneath this there are numerous layers of cells forming the *cortex*. Next to the cortex there is a zone of smaller and darker cells *p*, known as the *phloem*, through which the food passes in solution in the cell sap. Internal to the phloem one sees the *xylem* *x*, which consists of very large cells, whose walls are composed of altered cellulose or wood cellulose. The function of these cells is to give strength to the stem and to conduct water up from the roots. Dividing the phloem from the xylem is a zone of actively growing cells *cb*, known as the *cambium*. In the phloem are bundles of fibres *b* termed *bast fibres*, which run throughout the whole of its length. These bast fibres are the source of all multicellular fibres.

**Preparation of Flax Fibre.**—Since the bast fibres form an integral part of the stem, cemented to the surrounding tissues, they are not directly available for spinning, as is the case with cotton. They must first be separated from the rest of the stem. The first process in their preparation is *retting*. The object of this is to break down the structure of the stem and dissolve the cementing substances, such as pectates, which hold the various tissues together. There are three kinds of retting processes, viz.: (1) water retting, (2) dew retting, (3) chemical retting.

(1) *In water retting*, the stalks are tied in bundles and covered with water in a tank. Putrefactive fermentation, caused by bacteria, soon sets in. This gradually softens the stalks, owing to the destruction of the less resisting tissues and the dissolution of the intercellular cement. When the fermentation has reached the right stage the bast fibres can be separated easily from the rest of the stalk. If the bacterial action is allowed to proceed beyond this point the fibres may become damaged. To prevent this the stalks must be carefully inspected at intervals. This danger of over-retting, together with the fact that the process takes about three weeks to complete, are serious disadvantages, but these, in practice, are counterbalanced by considerations of cost. A difficulty in the process is that it is purely empirical, and it is not known with certainty what organisms are concerned in the fermentation. Many experiments are being conducted with the object of isolating the special bacteria or enzymes which bring about the result.

(2) *Dew retting* is similar in its action to water retting, but slower. The stalks are spread out on grass to ferment, and the necessary moisture is supplied either by dew or by occasional watering. Sometimes the fermentation is started by water retting, and the stalks are then laid out to complete the process by dew retting.

(3) *Chemical retting* consists in softening the tissues, by such means as boiling with acid or alkali, either with or without pressure, and then washing away the soluble bodies produced by the chemical action. This process is much quicker than either of the others.

After retting, the stalks or "retted flax" are passed between rollers to squeeze out the excess of liquor and soluble impurities, and are then washed and dried.

*Breaking* is the next operation. The dried stalks are crushed by passing them through pairs of horizontal fluted rollers, which break up the woody tissue (or xylem) into small fragments, leaving the less brittle bast fibres undamaged. After breaking, the crude fibres are separated from the broken fragments by a process termed *scutching*. This may be done by simply beating the broken stalks by hand till the fragments of woody tissue are entirely removed. The operation is, however, generally carried out by machines specially designed to produce a similar beating effect. The scutched flax is then *hackled*. Hackling is a combing process which finally separates the fibres and lays them parallel to one another. Hackled flax is then drawn out and spun in a similar manner to cotton.

**Microscopic Structure.**—Flax fibres vary in length from 1 to 3 inches. Each fibre is composed of a large number of fibrils consisting of cells joined together. These have an average length of about 1 inch and a diameter of from  $1/1800$  to  $1/1000$  of an inch. The fibre has the appearance of a straight tube with thick walls and a narrow but distinct lumen, Figs. 63 and 64. The end of the fibre appears to be pointed, while on the outer surface are longitudinal striations. A cross-section of the fibre is polygonal in shape. Many nodes or swellings are visible on the surface, giving the fibre a jointed appearance.

Where these joints occur, as well as at other points, there will often be seen transverse divisions across the fibre, placed somewhat obliquely to the longitudinal axis. Both joints and transverse striations are rendered more visible by mounting the fibre in iodine-sulphuric acid or zinc chloriodide. No natural twist can be seen, but the apparently rough surface and the jointed structure assist in spinning.

The cell-walls are very thick, and no cuticle is present. On this account the fibre when treated with Schweitzer's solution, although it swells up, does not give the globular swellings that cotton does.

Flax is quite easy to distinguish from cotton, but is liable to be confused with hemp, jute, or ramie. But jute contains lignocellulose and is stained yellow by aniline sulphate. Flax contains no lignocellulose.

Raw flax is brownish in colour. After bleaching it is white, soft, and lustrous. Its tensile strength is equal to that of cotton, but its elasticity is



Fig. 63.—Flax Fibres.



Fig. 64.—Single Fibres.

less. Its suppleness and spinning power are closely connected with the presence of a peculiar oil or wax. If this is removed completely, the fibres become brittle, rough, and lustreless. This is partly why natural retting is preferred to chemical processes. The latter, involving boiling with alkali, by removing the wax make spinning more difficult. In conditioning flax or linen the standard regain for moisture is 12 per cent. The count of linen yarns is based upon a hank of 300 yards, the number of hanks weighing one pound denoting the count. Flax and other multicellular fibres are rendered more suitable for spinning by a process termed *cottonizing*. This consists in passing the fibre through specially constructed tearing and crimping machines, or in treatment with strong solutions of caustic alkali. The object of these processes is to separate the fibre into its ultimate cells or fibrils, thus giving it a physical condition similar to that of cotton. Wool-like effects are said to be produced by treating flax with a solution of cellulose in nitric acid, while digestion with pancreatic ferments is claimed by another patent as producing a soft and lustrous effect.

**The chemical constituents** of flax are the same as those of cotton, *i.e.* cellulose, proteins and other amino compounds, pectins, oil and wax, mineral salts, and natural colouring matters. When pure, flax cellulose is identical with that of cotton, and gives all the same reactions. The impurities are much more difficult to remove than those of cotton, bleaching being very difficult to carry

out. The absence of cuticle, together with the difficulty of completely removing the oils, waxes, and colouring matters, makes it difficult to get a pure white without at the same time producing some oxycellulose. To avoid this, comparatively mild processes must be used, and the impurities removed gradually in successive layers or stages by repetition of some or all of these operations. For these reasons bleached flax generally contains sufficient impurities to give a yellow colour when immersed in a cold solution of potassium hydroxide.

### Ramie.

Ramie and *China grass* consist of the bast fibres from species of stinging nettle belonging to the natural order *Urticaceæ* and sub-division *Bœhmeria*. They are cultivated in China, Japan, India, South America, and other places. The plant or shrub grows to a height of from 4 to 8 feet; it is hardy, grows rapidly, and yields three or four crops a year. The preparation and properties of the fibre have been described fully by Marshall (*J. Soc. Dyers Col.*, 1922, **38**, 292), from whose paper the following details are taken.

The plants are cut down and decorticated, the bast fibres being separated in the form of ribbons, which are hung up to dry. The stems are simply soaked in water till they are soft, and then the outer portions (or bark) are scraped off by hand, by means of a knife, a ring, or the fingers. The composition of the decorticated fibre is given in Table XI.

TABLE XI.—COMPOSITION OF CHINA GRASS AND RAMIE.

	China Grass. Per cent.	Ramie. Per cent.
Ash . . . . .	2.87	5.63
Water . . . . .	9.05	10.15
Matter soluble in water . . . . .	6.47	10.34
Fat and wax . . . . .	0.21	0.59
Cellulose . . . . .	78.07	66.22
Pectins, etc. . . . .	6.10	12.70

The decorticated fibre is then subjected to a *degumming* process, which removes most of the impurities, leaving nearly pure cellulose. This is practically the same as that used for scouring and bleaching cotton, which will be described later. The microscopic appearance of ramie fibres is similar to that of flax, but they are coarser and more irregular, and have also a wider lumen (Fig. 65).

Bleached ramie is white and lustrous. It is one of the strongest of vegetable textile fibres, and is extremely durable; but it is rather deficient in flexibility and elasticity. It does not, therefore, bend easily, and unless it has been carefully treated has a tendency to break. The individual fibres do not adhere to one another as do those of cotton.

It has also a peculiar hairiness which, while enabling it to be worked with wool, renders it unsuitable for fabrics which have to be worn next to the skin.

The figures given in Table XII, and taken from Marshall's paper, show the relation of the physical properties of ramie to those of other fibres.



TABLE XII.—PHYSICAL PROPERTIES OF RAMIE AND OF OTHER FIBRES.

Property.	Ramie.	Flax.	Cotton.	Hemp.	Silk.
Tensile strength . .	100	25	12	36	13
Elasticity . . . .	100	66	100	75	400
Torsion . . . . .	100	80	400	95	600

Ramie may be spun alone or with cotton or other fibres. According to Marshall (*loc. cit.*), mercerization of ramie yarns, etc. gives an increased lustre and a loss of hairiness. But it has also another interesting effect. If mercerized ramie fibres are examined under the microscope (Fig. 66), it is seen that a large



Fig. 65.—Ramie Fibres.

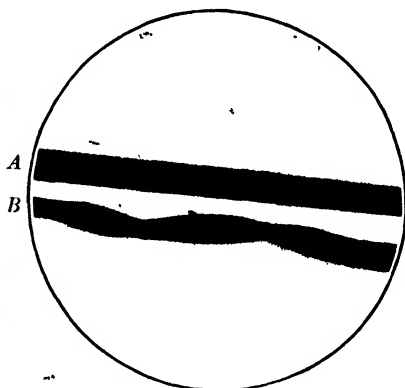


Fig. 66.—(A) Single Ramie Fibre mercerized under Full Tension.

(B) Single Ramie Fibre mercerized without Tension.

proportion of the loose fibres, especially the finer ones, have lost their comparatively straight cylindrical form, and have assumed a twisted appearance like that of cotton. This twist, however, is produced only when mercerization is carried out without tension. Ramie differs from cotton also in another particular. When mercerized without tension, there is no increase in tensile strength but a slight decrease. When mercerized under tension, both increased lustre and strength are observed, accompanied by loss of hairiness. Some of the fibres become partly twisted, others appear like unmercerized cotton fibres, but the larger proportion retain their original appearance. Mercerized ramie has also an increased elasticity and flexibility. Ramie has the same dyeing properties as cotton, except that it has a somewhat greater affinity for basic dyes.

### Hemp.

Hemp is derived from the bast fibres of the hemp plant, *Cannabis sativa*. It is grown chiefly in moderate and subtropical climates. It is cultivated not only for the sake of its bast fibres, but also on account of its seeds. The latter contain a narcotic principle, and are used for the preparation of *hashish*.

The fibres are separated from the plant in the same way as flax, the waste being used as tow. Hemp fibres are used largely in the manufacture of string and rope and of coarse unbleached textile fabrics. Its marked tensile strength renders it particularly suitable for these purposes. The finest varieties, such as Italian, have little colour, and can be spun alone or with other fibres. The dark colour and difficulty of bleaching the coarser kinds prevent their use to any great extent.

**Microscopic Appearance of Hemp.**—Hemp fibres are very similar to flax, but less regular, and the articulations are not so well marked. The lumen is rather broad and easier to see than in the flax fibre, and the ends of the fibres are rounded or blunt. Fig. 67 shows Italian hemp fibres, and is taken from a paper by Flatters (*J. Soc. Dyers Col.*, 1920, 36, 76).

A cuticle is present, and the fibre shows globular swellings like cotton when treated with Schweitzer's reagent. In this respect it differs from flax. A further distinction (Haller, *J. Soc. Chem. Ind.*, 1920, 39, 292A) is the action of sodium hydroxide solution. When treated with this reagent, flax swells uniformly, and the contents of the lumen show up distinctly, while the fibre substance becomes uniformly transparent. With hemp the contours appear irregular, the fibre non-transparent, and the wall of the lumen indistinct. The diameter of the flax fibre is increased by 85 per cent., that of the hemp fibre by not more than 25 per cent. The fibres of hemp are remarkable for their length, ranging from 1000 to 3000 mm. The ultimate fibrils are from 15 to 20 mm. long, and have a diameter of from 0.016 to 0.05 mm.

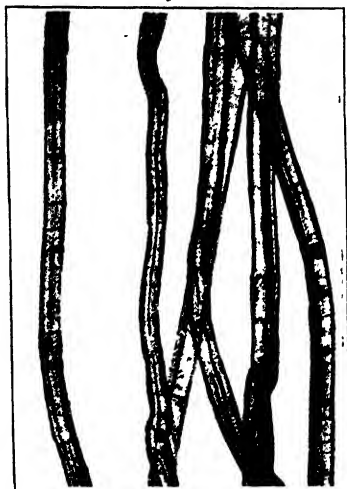


Fig. 67.—Italian Hemp Fibres.  $\times 75$ .

**Chemical Properties.**—Raw hemp has, as a rule, a marked brown colour. In the finer varieties the colour is less marked, and these can be bleached in the same way as flax. Bleached hemp is used as a substitute for flax, but its spinning power is not so great. Its constituents are the same as those of flax, except that it contains, in addition, a wood cellulose termed *lignocellulose*. This stains yellow with an aqueous solution of aniline sulphate or other salt.

### Jute.

Jute consists of the bast fibres from plants of the natural order Tiliaceæ, of which the lime tree is a member. It is cultivated largely in India. There are two important species, *Corchorus capsularis* and *Corchorus olitorius*. Both are annual herbaceous plants growing to a height of 5 to 14 feet. The fibre is separated by retting in a similar manner to flax. Jute is used chiefly for sack-cloth, coarse cloths, carpets, and in the manufacture of higher-grade fabrics.

**Microscopic Structure.**—Jute fibres are similar in appearance to flax and hemp, but are characterized by the irregularity of the lumen. This is caused by the cell-walls, which are at some places thick and at others extremely thin. The width of the lumen varies inversely with the thickness of the cell-walls,

sometimes occupying the greater part of the cell. Fig. 68 shows the appearance both of a bundle and of the ultimate fibrils.

**Properties.**—The fibres of jute are very long, averaging from 1500 to 3000 mm. The individual fibrils range from 1.5 to 4 mm. in length and 0.015 to 0.020 mm. in diameter. The tensile strength and elasticity of jute are comparatively low, being less than those of flax and hemp. Jute is usually brownish in colour, and has a considerable lustre. It is not very durable, and is gradually rotted by exposure to damp air or water, while fabrics made



Fig. 68.—Jute Fibres.

of jute are disintegrated by frequent washing. Chemically, jute differs from other textile bast fibres in containing chiefly lignocellulose. This is identified by the facts that it stains a yellow colour with aniline sulphate and crimson-red with phloroglucinol and hydrochloric acid. The latter reagent may be made by dissolving 1 g. of phloroglucinol in 10 ml. of alcohol or methylated spirit, and adding an equal volume of 10 per cent. hydrochloric acid just before use. The material to be tested is soaked in the reagent, and then warmed in a porcelain dish on the water-bath. Hemp, which is coloured slightly yellow by aniline sulphate, gives a brownish-red colour with phloroglucinol, while jute gives a deeper yellow and a crimson colour. Jute is difficult to bleach, since it is attacked by chlorine, especially in alkaline solutions. The best varieties, however, have comparatively little colour, and can be dyed without bleaching. Jute differs from other vegetable fibres in having a comparatively strong affinity for basic dyes.

## CHAPTER XII.

### ARTIFICIAL FIBRES.

**ARTIFICIAL** fibres may be of either vegetable, animal, or mixed origin. The vegetable fibres are known as *rayons* (or *artificial silks*), and are made from cotton, cotton linters, or paper pulp. The chief of these are Chardonnet or nitro rayon, Pauly or cuprammonium rayon, viscose and cellulose-acetate rayons. The principal artificial animal fibre is lanital, which is prepared from casein.

*Linters*, as mentioned in Chapter IX, consist of the short hairs which are left on the cotton seed by the process of ginning. They are removed subsequently, bleached by the methods used for cotton, and pressed into thin sheets. It is important that they should contain neither hydrocellulose nor oxycellulose.

*Wood or paper pulp* is obtained from the wood of the spruce tree, which grows chiefly in Scandinavia and Newfoundland. This is cut into small pieces or pulped, and heated under pressure with an aqueous solution of calcium bisulphite and sulphurous acid. This changes lignin into a soluble salt of lignin-sulphonic acid, and dissolves also other impurities. The residue is washed with water, bleached with chlorine or bleaching-powder, washed again, and pressed into thin sheets, which are used largely for the manufacture of paper and as a filtering material.

*Casein* is prepared from separated milk by treating it with an acid at pH 4 to 5. The precipitated casein is separated, washed with water, and pressed.

*Polymers*.—A recent addition to artificial fibres is a group spun from polymers. *Nylon* is a polyamide of hexamethylene-diamine and adipic acid, and *Vinyon* is produced by the co-polymerisation of vinyl chloride and vinyl acetate.

#### Nitro or Chardonnet Rayon.

Nitro rayon was made first by Chardonnet in 1884, and improved by Lehner and Bronnert. The starting-point is nitrocellulose.

When cellulose is treated with a mixture of nitric and sulphuric acids, it gives rise to nitrates of cellulose, the composition of which depends upon the conditions of the reaction. Thus with two molecules of nitric acid for each two  $C_6H_{10}O_5$ -units a dinitrate is obtained, in accordance with the equation:



Higher nitrates containing four to six nitro groups are powerful explosives, and constitute guncotton.

**Manufacture.**—Purified cotton (or linters) is treated with a mixture of nitric and sulphuric acids, at a temperature not exceeding 40° C., for from four to six hours. The excess of acid is then run off, and the nitrated cotton washed with water until free from acid. It is then hydro-extracted or pressed until it contains about 30 per cent. of water. The pressed nitrocellulose is

next dissolved in a mixture of equal volumes of alcohol and ether in a closed vessel provided with a stirring mechanism or in a closed rotating drum. The solution is filtered through paper pulp under pressure, and the filtrate kept in a closed vessel to allow air to escape and to promote "ripening." The solution is colloidal. When a colloidal solution is allowed to stand, its viscosity increases gradually to a maximum, and then begins to diminish. In order to obtain regular results in spinning, the solution must have a definite and constant viscosity, depending upon the nature of the thread required. The storing of the solution until it has this desired viscosity is termed *ripening*.

The ripened solution is filtered under pressure and spun. Spinning consists in forcing the viscous solution through fine orifices of about 0.1 mm. diameter, solidifying the extruded filaments, and collecting them on a bobbin or reel. When the spinning solution contains a volatile solvent, the filaments may be produced by evaporation of the solvent. This is termed *dry spinning*. In other cases the spinning orifice is immersed in a bath containing water and a coagulating agent, the filament being produced by precipitation. This constitutes *wet spinning*. A brief description of the apparatus used for spinning may be given:

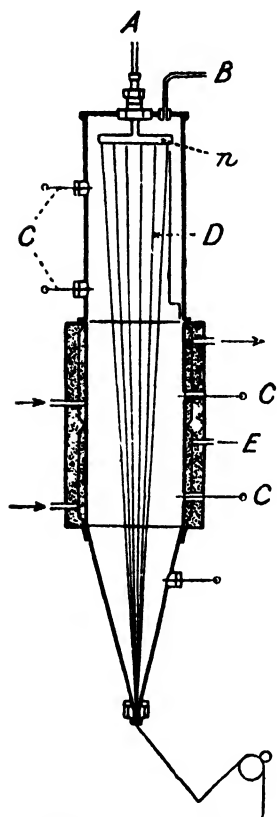


Fig. 69.—Dry-spinning Apparatus.

(1) *Dry Spinning*.—The apparatus (Fig. 69) consists of a metal chamber which tapers towards its lower end. The spinning solution enters through *A* to the spinneret *n*, which has a number of nozzles, and revolves round a vertical axis. The filaments *D* which are produced are gathered together to form a single thread at the lower end of the cone, whence they pass to the winding apparatus. Air enters the chamber at the lower outlet, and leaves at *B*, being heated as it rises by the hot-water jacket *E*; it then passes to the solvent-recovery apparatus. The temperature of the water is regulated by means of thermometers *C*.

(2) *Wet Spinning*.—The spinning solution passes through the tube *A* (Fig. 70) to the spinneret, which is immersed in a bath containing a solution of the precipitant. The coagulated thread *B* travels upwards to the bobbin *D*, which is actuated by the motor *C*. In centrifugal-box spinning (Fig. 71), used chiefly for viscose, the coagulated filaments (1) pass over a roller (2) through the funnel (3) into the cylindrical box (4), which rotates at a speed of from 5000 to 6000 revolutions per minute. The thread forms a cake inside the box, which is driven by a motor (7) and a driving spindle (6). The centrifugal box is used only in the manufacture of viscose. The funnel is given an up-and-down motion to distribute the thread in a spiral form in the box.

Both methods are used in the case of nitrocellulose. In dry spinning the solvent is recovered by condensing it in cresol, from which it is subse-

quently removed by distillation. In wet spinning a bath containing water and an electrolyte such as sodium sulphate is used. The nature of the filament varies with the process used. As a rule, filaments produced by precipitation have a smooth, round cross-section, whilst in those obtained by evaporation the cross-section is irregular or indented.

The bobbins are washed with water, partly dried, passed through a twisting machine, and reeled into hanks.

All kinds of nitrocellulose are very inflammable, and could not be used as such. When nitrocellulose is treated with a suitable reducing agent, the

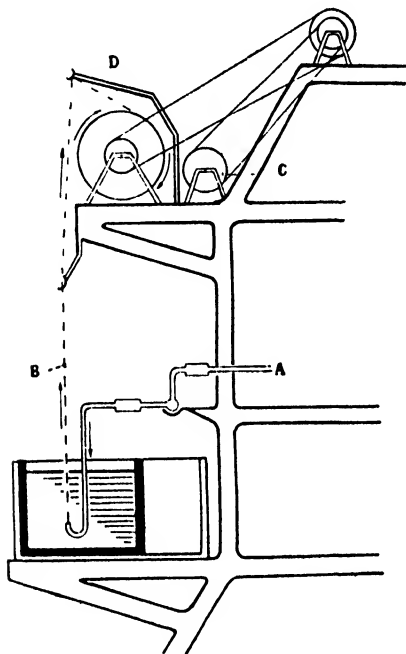


Fig. 70.—Wet-spinning Apparatus.

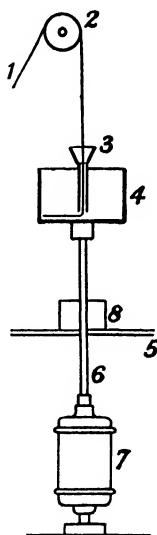
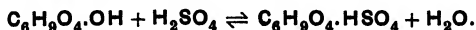


Fig. 71.—Apparatus for Centrifugal-box Spinning.

nitro groups are removed, and cellulose is regenerated. This is the next operation, and is known as *denitration*. The hanks are treated for about three hours with an aqueous solution of sodium hydrosulphide at 40° C. They are then washed, bleached, and dried. Denitration is never quite complete. A little nitrogen is always left, the amount varying from 0.05 to 0.1 per cent. This can be detected by the diphenylamine test, and serves for the identification of nitro silk. Traces of sulphuric esters of cellulose may be present also, formed in accordance with the equation :



If these are present, tenderness may result, since the reaction is reversible.

Nitro or Chardonnet rayon is sensitive to mechanical damage, and when wet loses some of its tensile strength. Owing to the presence of residual acid groups it has a distinct affinity for basic dyestuffs. It gives the reactions for

cellulose. Under the microscope it appears to be structureless, but shows longitudinal markings, which correspond to the irregular outline of the cross-section. These are illustrated in Figs. 72 and 73.



Fig. 72.—Nitro-rayon Filaments.



Fig. 73.—Cross-sections of Nitro-rayon Filaments.

It may be noted here that the counts of all kinds of rayon are expressed in terms of deniers.

### Cuprammonium Rayon.

The manufacture of cuprammonium rayon is based upon Schweitzer's discovery that cellulose is dissolved by a solution of copper oxide in ammonia. Attempts to utilize this discovery for the preparation of fibres were made by Depaïssis, but Pauly, in 1897, was the first to work the process on a commercial scale. Later developments were due to Bemberg.

**Manufacture.**—Cuprammonium rayon can be made from bleached cotton or linters. These, after bleaching, are washed with water, and pressed until they contain about 50 per cent. of water. The pressed residue is placed in a mechanical mixer together with cuprammonium solution, and kept at a temperature of about 5° C. until it is dissolved. The concentration is then adjusted to about 45 g. per litre, and the solution filtered under pressure. The cuprammonium solution may be made by passing air through a solution of ammonia containing copper turnings. The filtered solution of cellulose is de-aerated by exposure to a vacuum, and then kept in closed vessels to "ripen." When the required viscosity has been produced, the solution is again filtered, and spun by the wet-spinning method. The spinning bath may contain sulphuric acid, which neutralizes the ammonia and precipitates the cellulose. A better method is to use a bath containing sodium hydroxide and dextrose. The sodium hydroxide decomposes the cuprammonium compound, giving copper hydroxide, which is reduced to cuprous oxide by the glucose, the precipitate settling to the bottom of the bath. The filaments, which will still contain copper, are washed with dilute sulphuric acid, then with water, twisted, and reeled into hanks. The excess of ammonia and copper are recovered from the wash liquors.

**Stretch Spinning.**—Cuprammonium rayon is particularly suitable for a process termed *stretch spinning*, whereby filaments comparable in diameter

with those of natural silk can be obtained. The process depends upon slowly or partly coagulating the filaments, stretching them whilst still plastic, and then completing the coagulation.

**Properties.**—Cuprammonium products have a soft silk-like handle, especially if stretch spinning has been employed. The cross-sections of the

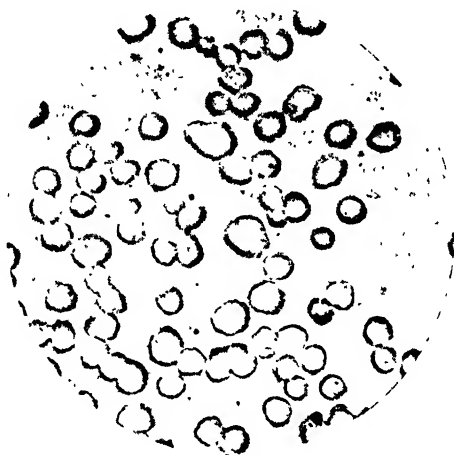
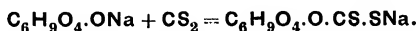


Fig. 74.—Cross-sections of Cuprammonium Rayon.

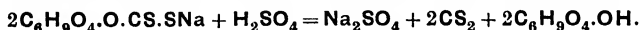
filaments have a rounded appearance (Fig. 74). This rayon has the same affinity for dyestuffs as cotton. Occasionally, traces of copper may be present, which may promote tendering.

### Viscose Rayon.

Viscose rayon consists of regenerated cellulose obtained by the decomposition of viscose. This substance, the sodium salt of cellulose-xanthic acid, was discovered by Cross in 1892, and is formed when alkali-cellulose is treated with carbon disulphide. The reaction is expressed by the equation:



Cross found that when a solution of viscose in sodium hydroxide is decomposed by an acid, cellulose is reproduced in accordance with the equation:



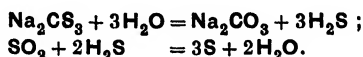
**Manufacture.**—Cotton, cotton linters, or wood pulp may be used, but as a rule the last-named is preferred. The sheets are soaked in a cold solution of sodium hydroxide of specific gravity about 1.3, in order to produce alkali-cellulose,  $\text{C}_{12}\text{H}_{20}\text{O}_{10}\cdot 2\text{NaOH}$ . The excess of sodium hydroxide is removed by pressure, and the residue ground to crumbs. These are kept in closed tins at a temperature of 25° C. for two or three days to ripen. During this process oxygen is absorbed, and depolymerization takes place. Oxidizing agents are added sometimes to assist the process. The ripened alkali-cellulose is placed in a revolving drum and treated with carbon disulphide. The alkali-cellulose combines with the carbon disulphide, swelling gradually to a viscous yellow mass, consisting of impure viscose. The yellow colour is caused by the



presence of secondary products, such as sodium thiocarbonate, formed by the action of sodium hydroxide on carbon disulphide:



The crude viscose is next dissolved in dilute sodium hydroxide solution having a concentration sufficient to give about 6·4 per cent. of sodium hydroxide and 7·5 per cent. of cellulose, water being added to produce a suitable viscosity. Sodium sulphite is added also to decompose sulphuretted hydrogen produced during spinning. The solution is filtered, and allowed to ripen until it has the required viscosity. It is then filtered, de-aerated, and spun by the wet process. The spinning bath contains an acid, generally sulphuric acid, and a salt such as sodium sulphate. The acid decomposes the viscose in the manner described above, and the salt coagulates the filament. Various salts or other assistants are added also to affect the nature of the regenerated cellulose. It will be seen, from the equation given above, that carbon disulphide is liberated during spinning. This is changed into sulphuretted hydrogen by hydrolysis, and then decomposed by the sodium sulphite in accordance with the equations:



The liberated sulphur remains in the filaments.

The filaments or threads are collected as a rule by a *centrifugal spinning box*, which rotates at a speed of 5000 revolutions per minute. This introduces a twist, and the threads are deposited in the form of a cake round the side of the box. These cakes are washed with water to remove acid and other soluble impurities, and then wound into hanks. The free sulphur is now removed by treating the hanks with a warm solution of sodium sulphide and washing with water.

**Properties.**—The microscopic appearance of viscose is similar to that of other kinds of rayon. The cross-sections are variable in contour, depending

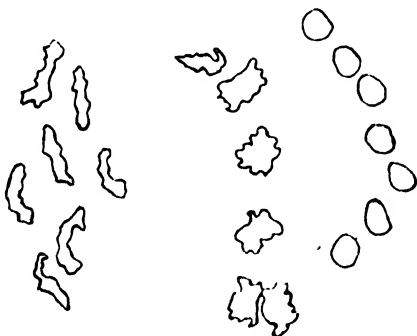


Fig. 75.—Cross-sections of Viscose Filaments.

on the method of spinning and the composition of the coagulating bath. Examples are seen in Fig. 75. Residual sulphur may be present, which affects the affinity for dyestuffs. This can be removed by treatment with a solution of sodium sulphide, and washing.

**Variations of the Process.**—Various additions may be made to the viscose solution for the production of special effects. The chief of these are—

- (1) *Hollow threads* are obtained by the addition of sodium carbonate to the viscose solution.
- (2) *Lustreless rayon.* By incorporating 0.1 to 0.5 per cent. of petroleum jelly in the viscose solution a soft finish like that of silk is produced. Other substances, such as finely ground titanium oxide, are used also.
- (3) *Filaments with some of the properties of animal fibres* may be made by adding a solution of casein or other protein to the viscose solution.

**Increasing Tensile Strength.**—The tensile strength of regenerated cellulose fibres is not enough for some purposes, particularly when wet. Many processes have been proposed to overcome this difficulty. They generally depend upon the addition of a swelling agent to the coagulating bath and applying stretch to the thread whilst it is in the plastic state imparted by the swelling agent. This gives a higher degree of orientation of the molecules, which is accompanied by greater tensile strength but diminished elasticity. The swelling agents which are used are mineral acids such as fairly strong sulphuric acid, or salts such as zinc chloride or thiocyanates.

**Non-creasing Effects.**—These are obtained according to the patented method of Tootal Broadhurst Lee and Company, by causing the material to swell in a mercerizing solution and impregnating it with an artificial resin, or with the components thereof, and completing the condensation subsequently by heat. The resin may be made of 100 parts of phenol by weight, 100 parts of 40 per cent. formaldehyde, and 4 parts of potassium carbonate, boiled together for five minutes and cooled rapidly.

**Staple Fibre.**—This consists of rayon filaments cut into definite lengths and spun into yarn. Messrs Courtauld's *Fibro* is a good example. It is supplied in different denier sizes and lengths (Table XIII). The finer fibres are spun

TABLE XIII.—SIZES OF RAYON STAPLE FIBRE.

Denier.	Length, in.
1.5	$1\frac{7}{16}$ and $1\frac{1}{2}$
3.0	$1\frac{1}{4}$ and 3
4.5	2 and 4
8.0	8

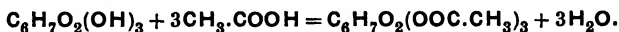
on cotton machinery, and the coarser on woollen and worsted machines. *Fibro* is either bright or matt, the latter being produced by adding titanium oxide to the viscose solution. It has a soft, warm handle, a silky lustre, and good covering power, durability, and dyeing properties.

*Rayolanda X* is a viscose fibre on the surface of which a synthetic resin has been deposited which is basic in reaction. This gives the fibre an affinity for acid dyes and other dyestuffs commonly applied to wool. The product is supplied in the form of staple fibre and is used for admixture with wool. It is possible to obtain solid dyeings or two-tone effects with wool dyes. There is an advantage in the use of this fibre in that shades of a higher degree of fastness

to washing can be produced than would be the case if a regenerated cellulose staple fibre which must be dyed with direct cotton dyestuffs were mixed with the wool. Rayolanda, when mixed with wool, also gives a handle more closely related to that of pure wool than is the case with regenerated cellulose staple fibres.

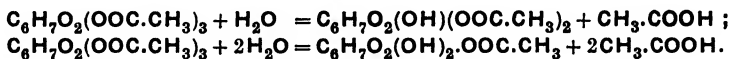
### Cellulose-acetate (Acetyl) Rayon.

Cellulose acetate was discovered by Cross and Bevan in 1894 during an investigation of the nature of cellulose. They found that when cellulose is heated with acetic anhydride, acetic acid, and a condensing agent such as zinc chloride, it reacts like other alcohols to give an ester. They thought that a tetracetate was produced, but later work showed that it was probably a triacetate. The reaction is represented by the equation:



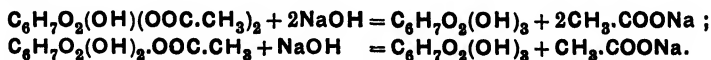
This triacetate is a white solid substance, insoluble in water, but soluble in chloroform or tetrachlorethane. It is known as *primary* cellulose acetate. Its solution in organic solvents has good waterproofing properties, but is not suitable for the manufacture of filaments. Primary cellulose acetate is a non-conductor of electricity, a bad conductor of heat, and not very inflammable.

When primary cellulose acetate is hydrolysed under controlled conditions, one or two of the acetyl groups are replaced by hydroxyl groups, thus:



The same results can be obtained by direct acetylation. These lower acetates are called *secondary* acetates. They are insoluble in chloroform, but readily soluble in acetone. They form the starting-point for the preparation of acetyl filaments. These lower acetates are used because the tetracetate is impervious to water, and could not be wetted down in a dye-bath; the hydroxyl groups of the lower acetates enable wetting to take place. After the acetylation of the cellulose (generally cotton) is complete, the acetate is precipitated by diluting the mixture with water. It is then washed with water and dissolved in a suitable organic solvent, and the solution filtered and allowed to ripen. Cellulose acetate may be spun by either dry or wet methods. In the latter the precipitating bath may contain various chemicals such as methyl or ethyl alcohol, acids, or salts.

**Properties.**—The microscopic appearance of cellulose-acetate rayon depends on the method used in spinning, and the contour of the cross-sections is very variable (Fig. 76). Acetyl rayon has a high lustre, and its tensile strength is not lowered by wetting to so great an extent as is that of the other forms of rayon. Owing to the presence of acid groups, it combines directly with many organic bases, and has a marked affinity for basic dyestuffs. On the other hand, its affinity for direct dyestuffs is comparatively small. When it is heated with solutions of caustic alkalis, sodium carbonate, or sodium silicate, saponification takes place, and cellulose is regenerated in accordance with the equations:



Acetyl rayon is more permanent than other kinds of rayon. Thus, when it is exposed to the action of water or bacteria, comparatively little damage occurs.

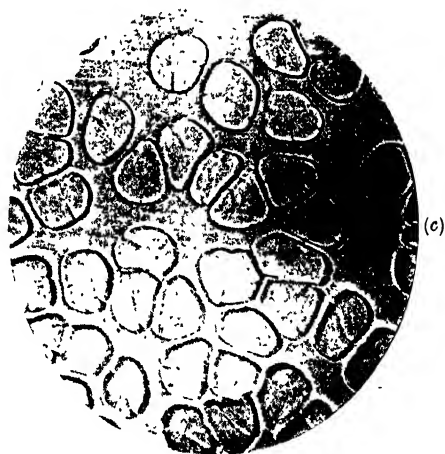
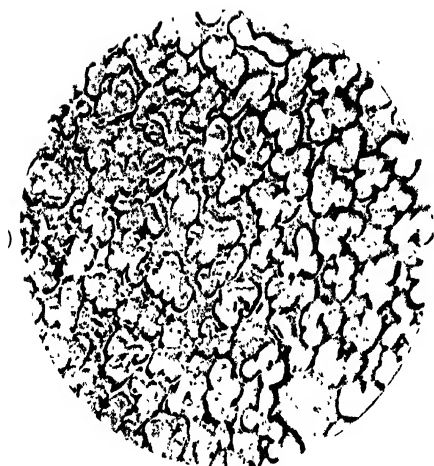
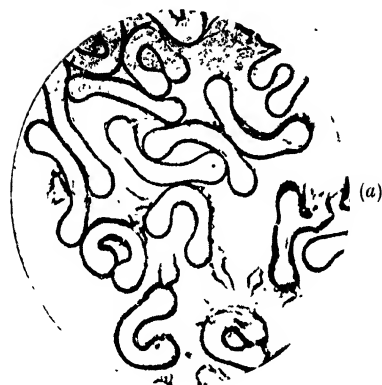


Fig. 76.—Cross-sections of Acetyl Filaments.

### Casein Fibres or Lanital.

**Manufacture.**—The raw material for the manufacture of lanital and other similar fibres, such as *triolan*, is casein obtained from separated milk. This is coagulated with an acid at pH 4.5, and the coagulated casein separated and pressed. It is then dissolved in dilute sodium hydroxide solution, and allowed to mature. The matured solution is spun into dilute sulphuric acid containing an electrolyte, such as sodium sulphate, and formaldehyde. The resulting fibres are treated again with formaldehyde, cut into short lengths, washed, and dried. They are then spun into yarn. Composite casein and viscose fibres may be made by mixing viscose with the alkaline solution before spinning.

**Properties.**—Lanital has a soft handle like that of wool, and consists essentially of casein. It differs from wool in containing only a small proportion of sulphur, and in the absence of cell structure. Its tensile strength is about one-third of that of wool, but its extensibility is nearly twice as great. It swells in cold water, losing 20 per cent. of its tensile strength. When treated with hot water, or distilled with water or dilute acid, formaldehyde is liberated. Heating with soap or alkalis causes considerable loss of tensile strength, and dyeing in an acid dye-bath has the same effect, especially at the boiling-point. Larose (*Canadian Text. J.*, 1936, 53, 45) gives the details of comparative tests made with wool and lanital reproduced in Table XIV. Qualitative tests for the identification of lanital have been described above, p. 66.

TABLE XIV.—PROPERTIES OF LANITAL AND WOOL.

Property.	Lanital.	Merino Wool.
Breaking strength at 60 per cent. humidity	8.2 g.	14 g.
Elongation at breaking-point . . . . .	80 to 100 per cent.	30 per cent.
Swelling in water . . . . .	18 per cent.	18 "
Swelling in 0.1N. sodium hydroxide. . . . .	86 "	60 "
Ash . . . . .	4.8 "	0.2 "
Sulphur . . . . .	0.7 "	3.2 to 4 per cent.

When casein fibres are mixed with wool they increase the tendency to felt. They find, therefore, a useful outlet in the felt industry. In textile fabrics, on the other hand, felting is often a disadvantage and, for this reason, particular care should be taken in dyeing wool casein mixtures.

**Nylon and Vinyon.**—The preparation and properties of these polymer fibres are described on p. 526.

## CHAPTER XIII.

### SILK.

SILK as a textile fibre possesses to a very high degree the properties of strength, elasticity, lustre, durability, and dyeing ability. It is, in fact, the nearest that we know to a perfect textile fibre. It consists of a solidified (or coagulated) viscous liquid secreted by the silk glands of the silkworm. It is made once only by the worm and for a special purpose, namely, to protect itself during its chrysalid state.

Silk has been cultivated in China since about 2600 B.C. at least, but its use as a textile fibre was known long before this. During the sixth century it was introduced into Europe by two monks, who carried away, secretly, a supply of silkworm eggs to Constantinople hidden in a hollow cane. It is now chiefly produced in Italy, France, China, and Japan. There are different varieties of worms producing silk, but nearly all the commercial forms belong to the species *Bombyx*, while the common silkworm is known as *Bombyx mori*. Inferior silk is also obtained from others without special cultivation. This, such as Tussur silk, is known as *wild silk*. *Bombyx mori* feeds chiefly on mulberry leaves, while the wild varieties live on various trees, such as oak.

The following list of the various kinds of *Bombyx* (i.e. cultivated) silkworms is taken from *Chambers's Encyclopædia*:

"*Bombyx mori* (Linnæus).—The common silkworm, domesticated in China, Bokhara, Afghanistan, Cashmere, Persia, South Russia, Turkey, Egypt, and Algeria, Italy, France, and Spain, in all which countries it produces but one crop annually, spinning the largest cocoon and the best silk of a golden yellow or white.

"*B. texor* (Hutton).—The Boro Poloo of Bengal, domesticated in South China and Bengal; an annual only, producing a white (sometimes yellow) cocoon of a different texture and more flossy than *B. mori*.

"*B. sinensis* (Hutton).—The Sina, Cheena, or small Chinese monthly worm of Bengal, introduced from China, and partially domesticated in Bengal; produces several broods in the year; cocoon white and yellow.

"*B. crassi* (Hutton).—The Nistri or Madrassee of Bengal, introduced from China, and domesticated in Bengal; yielding seven or eight broods of golden yellow cocoons in the year of larger size than *B. sinensis*.

"*B. fortunatus* (Hutton).—The Desi or Chota Poloo of Bengal; yields several broods annually, spinning the smallest cocoon of a golden yellow colour.

"*B. aracanensis* (Hutton).—The Burmese silkworm, domesticated in Arakan, said to have been introduced from China; yields several broods annually; cocoons larger than the Bengal monthly species.

"*Theophila huttoni* (Westwood).—The wild silkworm of the north-west Himalayas, feeding on the indigenous mulberry in the mountain forests.

"*T. sherwilli* (Moore).—The wild silkworm of the south-east Himalayas.

"*T. bengalensis* (Hutton).—The wild silkworm of Lower Bengal, discovered in the neighbourhood of Calcutta, feeding on *Artocarpus lacoocha*. Found also at Ranchee, in Chota Nagpore.

"*T. religiosa* (Helfer).—The Joree of Assam and Deomooga of Cachar. Feeds also on the ber tree (*Ficus bengalensis*) and the peepul (*F. religiosa*).

"*T. mandarina* (Moore).—The wild silkworm of Chekiang, North China; said to feed on wild mulberry trees, spinning a white cocoon.

"*Ocinara lactea* (Hutton).—Mussooree, north-west Himalayas; feeds on *Ficus venosa*, spinning a small yellow cocoon, yielding several broods during the summer.

"*O. moorei* (Hutton).—Mussooree; also feeds on *F. venosa*, as well as on the wild fig, spinning a small white cocoon. It is a multivoltine.

"*O. diaphana* (Moore).—Khasi Hills.

"*Trilocha varians* (Walker).—North and South India."

**Sericulture.**—The eggs are washed and hatched in an incubator. The period of incubation is about ten days. The temperature of the incubator is at the commencement adjusted to 64° F. (17·8° C.), and raised gradually to 82° F. (27·8° C.). As the worms are hatched they are transferred to frames, and fed on chopped mulberry leaves. Fresh air and cleanliness are essential to the welfare of the worm, as it is subject to many diseases. Overcrowding also

must be avoided, while the food must be so distributed that every worm may get its proper share.

The diseases of the silkworm were studied first by Pasteur. They are caused by fungi, bacteria, or parasites. The more important are *muscardine*, *pebrine*, *flacherie*, *guttine*, and *grasserie*. Muscardine is due to a fungus which kills the worm before it can develop into a moth. Pebrine, flacherie, and guttine are the result of infection by a bacillus. All these diseases are transmitted from worm to worm, and, if not recognized in the early stages, may cause great mortality.

The worm eats continuously, a thousand requiring about 85 lb. of leaves in all. It grows rapidly, attaining, when mature, a length of from 3 to 4 inches. It changes its skin four times between birth and

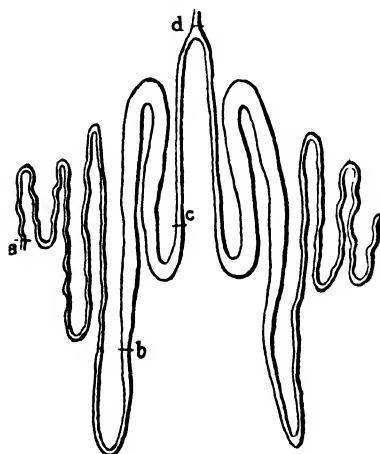


Fig. 77.—Silk Glands.

maturity. After the fourth change the worm stops eating and becomes restless. It is then placed on twigs, where it begins to enclose itself in a *cocoon* of silk. Care must be taken to see that each worm spins its own cocoon, and that two or more do not become mixed. The silk is produced by two glands, one on each side of the body of the worm. These, when the worm is mature, occupy a considerable part of the body, and are filled with a viscous liquid. From each gland a duct leads to a common orifice in the head of the worm. By muscular action the worm ejects the viscous liquid silk. The two liquid threads, which are termed *brins*, unite at the common orifice, the spinneret, forming a double thread known as a *bave*. As the liquid silk comes into contact with the air it coagulates or solidifies.

The above diagram (Fig. 77) illustrates the method of formation of these double threads (Georgievics, *Chemical Technology of Textile Fibres*, p. 29).

The portions *a*, *b* represent probably the actively secreting portions of the gland, the thicker parts *b*, *c* forming a reservoir or store. The capillary ducts commencing at *c* lead to the common orifice at *d*.

The silkworm spins the whole of its cocoon without a stop. Thus the silk consists of one continuous thread. A cocoon may contain 3000 yards of silk, about 1000 cocoons being required to give 4 ounces of silk. The process of spinning takes three or four days. When it is complete the worm forms a final skin, and changes into a *pupa*, which is either male or female in sex. The cocoons containing the former are somewhat cylindrical in shape and smaller than the oval cocoons which produce female moths. The cocoon contains approximately

Water	.	.	.	.	.	68.0 per cent.
Silk	.	.	.	.	.	14.5 „
Pupa	.	.	.	.	.	17.5 „

As will be seen later, each thread or brin consists of two distinct parts, *viz.* (i) a somewhat dense cylindrical core, which constitutes about 75 per cent. of the fibre, and is composed of true silk or *fibroin*; (ii) an outer and less opaque sheath composed of *silk-gum* or *sericin*.

It was thought, at one time, that the silk glands contained a single fluid which became oxidized at its surface as it issued from the spinneret, thus forming a superficial layer of sericin. Other observers held that the silk glands contained two distinct fluids, which when solidified formed sericin and fibroin respectively. Thus Georgievics states that if the silk gland be cut through at its thickest part, it is found to consist of two distinct portions: an internal transparent layer and an external sheath or stratum, which is colourless, greenish, or yellow according to the breed of the silkworm, and which occupies about one-quarter of the total volume of the gland. This outer portion forms sericin, and the inner fibroin. It is difficult, however, to understand how a single gland can secrete two fluids, simultaneously, which differ so much in physical and chemical properties as sericin and fibroin. Two distinct glands would appear to be necessary, and later researches indicate that this is the case. Placed near the head of the worm are a second pair of glands with ducts opening at the spinning orifice. As the fibroin issues from the silk glands it is covered with a layer of sericin secreted by the second pair of glands.

There is uncertainty, also, as to the way in which the liquid secretion coagulates or solidifies. That it cannot be mere drying is shown by the fact that no water is lost during the process; moreover, it will take place under water. It has been suggested that coagulation is caused by an enzyme, but if it were, the process would probably be retarded by heat, whereas it is accelerated. Further, it will take place in the presence of bodies such as potassium cyanide, which are known to destroy enzymes.

Light has been thrown on the process by Foa (*J. Soc. Chem. Ind.*, 1912, 31, 224), who extracted and examined the contents of the silk glands of a large number of worms. He found that the silk in the aqueous extract of the glands is present as an electronegative colloid, which gives a biuret reaction. The solution coagulates slowly on standing, or instantly on the addition of traces of acetic or other acid. Coagulation is accelerated, also, by heating, freezing, and remelting, and by mechanical strain. Foa attributes the natural coagulation of silk, as it is spun by the worm, to the mechanical strain exerted upon the viscous liquid as it is ejected from the spinning orifices.

The cocoons are now sorted. Some of the best, both male and female, are kept for breeding purposes. After a period of hibernation the pupa



changes into a moth with four wings, six legs, and two antennæ. It secretes a fluid which softens the silk, and pushes its way out of the cocoon. Its wings, which at first are immature, grow very quickly, and in a short time the moth becomes mature and able to fly. It then mates, the female lays its eggs, and both male and female die.

The remainder of the cocoons are baked or gently heated, to kill the pupa, after which they are separated into (i) best cocoons suitable for *organzine*, (ii) inferior cocoons for *tram*, and (iii) damaged, double cocoons, etc. for *spinning*. The cocoons are softened in warm water. Several free ends are collected by stirring gently with twigs. These are passed through an *eye*, and wound together. As they cool the different strands stick together, forming a single thread of *raw silk* or *grège*. The number of strands depends upon the count required.

According to Loewe's patent, the unwinding of the cocoons is rendered easier by previously soaking them in a dilute alkaline solution to which some soap has been added, this treatment being followed by washing with acidulated water. The silk obtained from a single cocoon varies in quality with its position. The outside layer is coarse and rough, and is termed *floss* or *waste*: it is collected separately for spinning. The innermost layers also are poor, owing probably to increasing exhaustion of the worm, and form also waste. Waste silk is separated into long fibres (*florette*) and short fibres (*bourette*). The best silk is found near the centre of the cocoon.

Thus, in the case of *Bombyx mori*, we have—

	Near Outside.	Centre.	Inside.
Diameter . . .	1/790 in.	1/900 in.	1/700 in.
Elasticity . . .	13.3	24.3	24.7
Strength . . .	6.25 g.	10.2 g.	9.0 g.

**Microscopic Structure.**—A thread of raw silk from the cocoon, *i.e.* a bave, consists, at first sight, apparently of two solid, cylindrical, structureless threads. These are seen in Fig. 78. The two threads or brins are generally



Fig. 78.—Raw Silk.



Fig. 79.—Ruptured Fibres.

stuck closely together, but in places they will be found to be separated. A thread from a skein of raw silk will, of course, show a number of these compound threads.

Careful focussing will show that each single thread or brin consists really of two portions, namely: (i) an inner cylindrical dense core, and (ii) an outer sheath. The inner core is the true silk, and is composed of the substance termed *fibroin*. The outer sheath consists of sericin or silk-gum. It is this substance which causes the two brins to adhere to each other, and which, becoming soft in warm water, allows their being wound together to form a compound thread. If a little of the raw silk be boiled with soap and water for about half an hour, the silk-gum will be removed. The residue consists of fine lustrous white threads of fibroin or true silk. If these are examined microscopically they appear to be solid, cylindrical, and structureless (Fig. 78). But they are in reality made up of a large number of very fine filaments or fibrils. When a thread of silk is treated with a solution of an alkali, or, still better, when it is boiled with soap and water and pounded in a mortar, these fibrils may sometimes be seen here and there in little tufts protruding from the thread, or as small knots. These may be seen in Fig. 79. These tufts or knots of fibrils are of importance in silk-dyeing. They are produced sometimes accidentally in handling or treating the silk. They do not take up dyestuffs as does the rest of the silk, and hence give rise to light-coloured spots or patches. This point will be referred to again later.

**Composition of Raw Silk.**—Besides the fibroin and sericin, raw silk contains small quantities of mineral matter, traces of fat and colouring-matter, and, of course, water. Its average composition is

Silk-gum or sericin . . . . .	22 to 25 per cent.
Fibroin or true silk . . . . .	67 to 62·5 „
Water . . . . .	10 to 11 „
Salts, etc. . . . .	1 to 1·5 „

**Definitions.**—Before proceeding to the study of the constituents of silk, it will be desirable to explain certain terms which are made use of, some of which have been mentioned already.

*Thrown silk* consists of two or more threads of raw silk (also called *reeled silk* or *grège*) thrown together and slightly twisted (Fig. 80). It is used for making both organzine and tram silk. The counts of thrown silk are expressed either in deniers or in Manchester thrown-silk counts, *i.e.* drams per 1000 yards.

*Organzine* is, as noted above, made from the best cocoons. It contains two or more threads. Each of these is composed of several threads of raw silk twisted slightly together. These are then doubled together, and retwisted in the opposite direction to the twist of the component threads (Fig. 80). Organzine is used for the warp threads of fabrics where tensile strength is required. Its counts are expressed in deniers.

*Tram* (Fig. 80) is the product of the second-grade cocoons. It is made, like organzine, from two or more single threads slightly twisted and then doubled; but the doubled thread is only very slightly twisted. Tram silk has less tensile strength than organzine, but more fullness owing to the twist being less. It is used for the weft threads of fabrics, in which filling power is of more importance than tensile strength. Its counts are expressed in deniers.

*Waste Silk.*—This includes the outer and innermost portions of the cocoons, cocoons which have been spun together, those damaged in baking, steaming, or reeling, or which have been used for breeding, and all waste ends. It is used for making different kinds of “spun” silk.

*Spun Silk.*—The waste silk is carded like cotton, and then spun. Under the microscope a thread of spun silk (Fig. 80) looks very similar to one of cotton, *i.e.* the short fibres are all twisted together round a common longitudinal axis.

The term "spun silk" is, however, reserved for that which is spun from waste from which the silk-gum has been completely removed by a process termed *boiling off*. That is, spun silk consists of fibroin. When the waste silk is spun without removing the sericin, the product is termed *chappe*. But *chappe* may be subdivided into (a) *florette*, which is made from the longer fibres obtained by carding or combing the waste; and (b) *bourette*, made from the shorter fibres. The counts of spun silk are the same as those of cotton

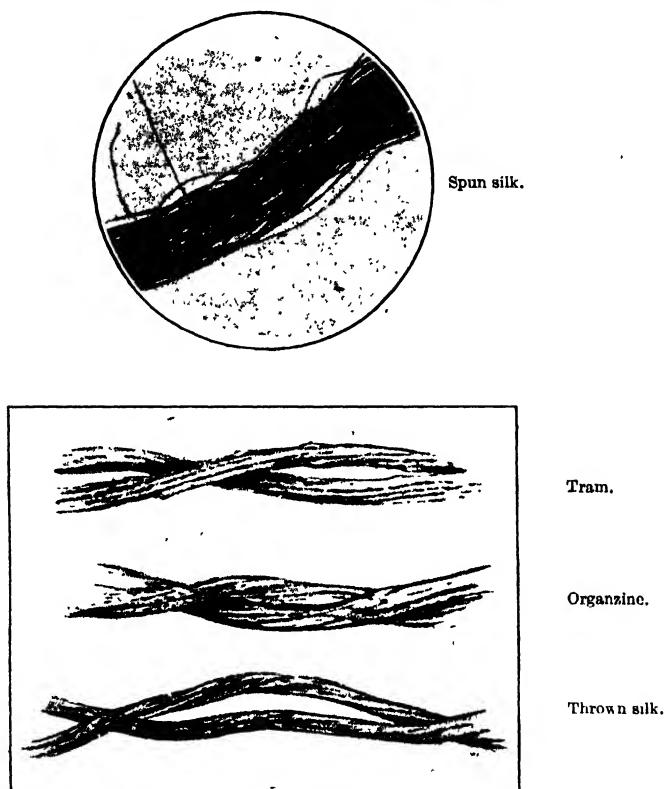


Fig. 80.—Spun Silk, Tram, Organzine, and Thrown Silk.

yarns, i.e. the hank contains 840 yards, and the count is the number of hanks required to make one pound in weight.

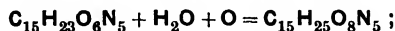
**Properties of Silk.**—Raw silk varies in colour from white to yellow, green, or brown, according to its origin, and the food upon which the worm has been fed. The colouring matter is contained chiefly in the silk-gum or sericin, and is removed when the silk is degummed by boiling off. In the case of some wild silks, like Tussur, the colour is distributed in the fibroin also. The specific gravity of silk is 1.33 to 1.34. It is very hygroscopic, being able to take up 30 per cent. of water when exposed to a damp atmosphere. The regain for moisture is 11 per cent. Conditioning is very important in the case of silk, and bales of raw silk rarely change hands without a certificate showing the weight of silk at correct condition present. Silk is a bad conductor, and, when dry, quickly becomes charged with electricity when rubbed. The diameter of

the fibre varies from 1/600 of an inch in the case of wild silk down to 1/2400 of an inch for the highest types of cultivated silk. There is no standard length, the fibre being continuous, as already stated, from beginning to end of the cocoon.

Its tensile strength is very great, being nearly equal to that of iron wire of the same diameter. Its elasticity varies from 20 to 30 per cent. The elasticity is increased by water, but the tensile strength of damp or wet silk is less than that of dry. It absorbs many substances from their aqueous solutions, such as tannic acid, sugar, metallic salts, and has a great affinity for dyes. The various systems by which the count is determined and expressed have been described in Chapter VIII.

Raw silk, as we have seen, consists of (i) sericin or silk-gum, (ii) fibroin or true silk, and (iii) traces of fat and mineral matter. The mineral matter never exceeds 1 per cent. The sericin varies from 16 to 28 per cent, according to the origin of the silk.

**Sericin**,  $(C_{15}H_{23}O_8N_5)_n$ , may be prepared from raw silk by heating it for some time, under pressure, with water. By this means a solution of the silk-gum is obtained, together with some protein. If the solution be made faintly acid with acetic acid and heated to coagulate the dissolved protein, this may be removed by filtration. The sericin may be obtained from the filtrate by concentrating on the water-bath and adding alcohol, which precipitates the gum. If this be filtered off and dried, a brownish powder is obtained, which swells up with cold water, and dissolves slowly in hot water. Sericin resembles gelatin in many of its properties, but, unlike gelatin, its aqueous solutions do not set to a jelly. It dissolves readily in hot soap and water or in a hot solution of sodium carbonate or other alkali. Like gelatin a solution gives precipitates with tannic and picric acids, and insoluble compounds with bromine and chlorine. But, unlike gelatin, it is thrown down by Millon's reagent and potassium ferrocyanide, if the solution be neutralized or made faintly acid with acetic acid. In the latter respects sericin resembles a protein. Like gelatin it has both acid and basic properties. It contains more oxygen than fibroin. This has given rise to the suggestion that it is produced by a process of oxidation at the surface of the exuded thread, in accordance with the equation:



but this view is not confirmed by the experiments of Foa, which have already been referred to.

Sericin combines with formaldehyde to form, on drying, an insoluble compound like that obtained with gelatin and proteins. This reaction is made use of for preventing loss of gum during dyeing and other operations. Prolonged boiling with dilute sulphuric acid resolves sericin into a mixture of simple amino compounds, which include about 5 per cent. of tyrosine,  $HO.C_6H_4.CH_2.CH(NH_2).COOH$ , and 10 per cent. of serine,  $HO.CH_2.CH(NH_2).COOH$ . It is of interest to notice that gelatin when treated in the same way gives no tyrosine, but chiefly glycine,  $NH_2.CH_2.COOH$ , and leucine,  $(CH_3)_2CH.CH_2.CH(NH_2).COOH$ . Hence it is believed that sericin contains aromatic nuclei, while gelatin does not.

Sericin is very readily soluble in alkalis, and is rendered soluble in water by pancreatic ferments. It is possible to degum silk, leaving the fibroin unattacked, by limited enzyme action. In preparing fibroin, or boiled-off silk, from raw silk, the sericin or gum is removed by means of a solution of soap. The solution of sericin thus obtained is highly colloidal, and is used in silk-dyeing as a levelling agent, under the name of *boiled-off liquor*, or *bast soap*. Not only is most of

the natural colour removed with the sericin, but there is also a considerable loss of both tensile strength and elasticity, amounting to about 30 per cent.

The process of "boiling off" will be described later. Silk is used both in the raw state and after boiling off. There are two varieties between raw and boiled-off silk, *viz.* *souple* and *écru* silk.

**Souple silk** is raw silk from which only 8 to 12 per cent. of the gum has been removed. It is suitable for wefts and dyeing and loading, but it loses the remainder of its gum when boiled.

**Écru silk** is raw silk from which only from 3 to 4 per cent. of the gum has been removed, by washing in lukewarm water or soap solution. It is used for the same purposes as *souple*.

Since the percentage of matter soluble in soap solution may vary in silk from 16 to 28 per cent., it is possible to increase artificially the proportion of impurities. This makes it desirable to establish limits between which the

TABLE XV.—IMPURITY LIMITS FOR SILK.

	Minimum, per cent.	Maximum, per cent.	Mean, per cent.
Matter soluble in—			
3 per cent. soap solution . . . . .	21.449	25.913	22.885
Distilled water at 55° C. . . . .	0.447	1.053	0.617
Ether . . . . .	0.104	0.451	0.275
Ash . . . . .	0.726	1.903	0.853

TABLE XVI.—EFFECT OF WATER CONTAINING EXTRACTIVES ON SILK.

	Water containing Extractives, per cent. by weight.	Ordinary Water, per cent. by weight.
Loss on boiling off . . . . .	22.63	18.85
Soluble matter at 55° C. . . . .	3.83	0.18
Soluble in ether . . . . .	0.56	0.29
Ash . . . . .	1.14	0.82

TABLE XVII.—COMPOSITION OF DIFFERENT VARIETIES OF SILK.

Variety.	Loss on Washing, per cent. by weight.	Loss on Boiling Off, per cent. by weight.	Soluble in Ether, per cent. by weight.	Ash, per cent. by weight.
White Kutais . . . . .	0.57	22.16	0.55	0.83
White Turkestan . . . . .	0.32	21.44	0.31	0.91
Yellow Adrianople . . . . .	0.54	24.88	0.35	0.88
Yellow Greek . . . . .	0.69	24.64	0.26	0.91
White Chinese crosses with Yellow Italian . . . . .	0.59	22.48	0.39	0.81

proportions may vary naturally. The Milan Commission on Silk (*J. Soc. Chem. Ind.*, 1906, **25**, 687) give the figures reproduced in Table XV. The presence of extractive matter from the chrysalides in the water used for unwinding the cocoons affects the results considerably, as is seen from Table XVI. According to the same report, different varieties of silk give approximately the results set out in Table XVII. The determination of matter soluble in water at 50° to 55° C. is of importance, since it indicates the presence of matters such as soap, glycerin, dextrin, glucose, and borax, which may have been added to the silk to increase its weight. A high ether extract would be suspicious, while the ash should not exceed 1 per cent.

**Fibroin** is a true protein. It is insoluble in water, dilute solutions of soap or alkali, and may be prepared from raw silk by removing the sericin with a hot solution of soap in water. Pure fibroin can be obtained by heating silk with water under pressure, washing the residue with hot water, drying, and extracting with alcohol and ether. Fibroin is, like other proteins, an amphoteric colloid, its iso-electric point being pH 3.8. When hydrolysed with either acids or alkalis it gives, finally, a mixture of amino acids, which include tyrosine, serine, alanine, glycine, and phenylalanine. Little is known of its structure, but according to Astbury (*J. Soc. Dyers Col.*, 1936, **52**, 306) it consists of fully extended polypeptide chains approximately parallel to the fibre axis. It forms an insoluble compound with formaldehyde, and gives all the general reactions of proteins. It can be distinguished from sericin by staining with picrocarmine. According to Denham and Dickinson (*J. Soc. Dyers Col.*, 1936, **52**, 94) a 0.1 per cent. solution of this dye gives a deep red colour with sericin and a pale yellow colour with fibroin. If 0.1 per cent. of sulphuric acid be present, the colours are dark brown and yellow respectively. Zimmermann's reagent (phthalaldehyde and hydrochloric acid) gives no colour with fibroin. These tests are useful for measuring the completeness of a degumming process. Fibroin, like sericin, dissolves in cold concentrated hydrochloric acid. It dissolves also in solutions of sodium hydroxide, Loewe's reagent, or ammoniacal nickel hydroxide. It is soluble in concentrated aqueous solutions of various salts, such as zinc chloride, lithium bromide, and calcium thiocyanate. Fibroin adsorbs a considerable quantity of tannic acid, stannic chloride, and other salts from their aqueous solutions, and this property is made use of in the weighting of silk. It has also a marked affinity for basic, acid, and direct dyestuffs. It is dissolved by proteolytic enzymes, but less readily than sericin.

**Action of Heat on Silk.**—Silk may be heated to a temperature of 140° C. for a short time without decomposition, but prolonged heating causes discoloration and loss of tensile strength. This is accompanied by loss of nitrogen in the form of ammonia.

**Action of Water.**—Prolonged boiling with water reduces both the lustre and the tensile strength of silk, these changes being very rapid at temperatures above 100° C.

**Action of Light.**—Prolonged exposure to sunlight or a short exposure to the light from a fadometer lamp reduces the tensile strength of silk. The presence of traces of iron or copper accelerates this action. Mineral acids such as hydrochloric act in the same way, but alkalis retard photochemical decomposition. When silk is exposed to the action of ultra-violet light, even for a comparatively short time, the loss of tensile strength is very marked, as is also the decrease in extensibility. Exposure for eight hours gave the results (Trotman and Bell, *J. Soc. Chem. Ind.*, 1936, **55**, 325r) shown in Table XVIII.

TABLE XVIII.—EFFECT OF LIGHT ON SILK.

	Tensile Strength, in lbs.	Extensibility, per cent.
Unexposed . . . . .	7.85	11.1
Exposed to filtered light . . . .	6.80	9.8
Exposed to unfiltered light . . .	3.83	5.4

**Detection of Damage.**—All kinds of damage due to chemical agencies can be detected and measured by the method of Trotman and Bell (*J. Soc. Chem. Ind.*, 1935, **54**, 141T; 1936, **55**, 325T), which depends on the fact that any kind of chemical damage affects the viscosity of a solution of the sample in a suitable solvent. The best solvent is a solution of zinc chloride in water having a density of 1.67, filtered through glass-wool. The method is as follows: A 2.5 per cent. (wt./vol.) solution of the sample is made by treating a weighed quantity with the required volume of the solvent in a stoppered bottle. This is placed in an incubator at 37° C. for exactly six hours. The bottle is then removed and cooled to 20° C. in water, and the viscosity of the solution is measured by a viscosimeter of the pipette type surrounded by a water-jacket kept at a temperature of 20° C. The viscosity is compared with that of water at the same temperature. It was found that undamaged silk gives a viscosity of from 3.0 to 3.3 compared with water.

The following experiments show the effect of light under different conditions on degummed silk. The viscosity of the unexposed sample was 3.1 compared with water. Samples treated in different ways were exposed to the light from a fadometer lamp for 24 hours, dissolved in zinc chloride solution, and tested (Table XIX). It will be noted that the presence of sodium hydroxide protects the silk to a considerable extent, whilst acids and metals which act as catalysts have the opposite effect. The protective action of alkali has been observed also by Harris and Jessup (*U.S. Bur. Stand. Res. J.*, 1931, **7**, 1179), who found that it was greatest at pH 10.

TABLE XIX.—EFFECT OF VARIOUS TREATMENTS ON SILK.

Method of Treatment.	Viscosity after Exposure to Fadometer (Water = 1.00).
Degummed with soap . . . . .	2.27
Method unknown . . . . .	2.00
Dyed with acid orange . . . . .	2.22
"  "  methylene blue . . . . .	2.03
"  "  benzopurpurine . . . . .	2.20
Wetted with 0.1N-NaCl and dried . . . .	1.61
"  "  0.1N-NaOH " " " " . . . . .	2.61
"  "  0.1N-H <sub>2</sub> SO <sub>4</sub> " " " " . . . . .	1.40
"  "  FeCl <sub>3</sub> (1 in 1000) and dried . .	1.42
"  "  CuSO <sub>4</sub> (1 in 1000) " " " " . .	1.90

**Action of Acids.**—As mentioned above, cold concentrated mineral acids dissolve silk readily. The solubility of silk in hydrochloric acid may be made

use of to determine the percentage present in a silk-wool mixture. When only traces of mineral acids are dried into silk tenderness results, and the material may disintegrate gradually to a powder. Boiling with dilute mineral acids also produces tenderness; hence a weak acid such as acetic acid is used in dyeing. With nitric acid a yellow colour, due to xanthoproteic acid, is produced. The effect of drying 0.1N. hydrochloric acid into silk is seen from the following figures:

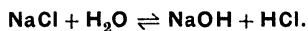
Viscosity of original silk	.	.	.	.	.	3.3
Viscosity after treatment with 0.1N.-HCl	.	.	.	.	.	1.85

When weak acids such as acetic or tartaric acid are dried into silk, they produce an effect termed *scroop*, but this is dependent upon the presence of a little soap.

**Action of Alkalis.**—Cold concentrated solutions of caustic alkalis appear to have little effect when the time of contact is very short and is followed by thorough washing. Crimped effects can be produced in this way by the mercerization of mixed cotton and silk fabrics. When a sample of silk was wetted with 0.1N. sodium hydroxide solution, squeezed, and dried, the viscosity of the zinc chloride solution fell only slightly, *viz.* from 2.95 to 2.9.

Prolonged contact with cold concentrated caustic soda solution results in disintegration and solution. Dilute solutions dissolve silk rapidly at the boiling-point. Alkaline carbonates act in a similar manner but more slowly. When small quantities of sodium hydroxide are dried into silk, the lustre is affected, but there is no loss in tensile strength, and the viscosity of the zinc chloride solution is not affected. The presence of alkali assists the production of ruptured fibres referred to above, which are termed *flocons* or *pelotons*, although the principal factor is friction or other mechanical agency. The formation of these flocons is favoured by processing at a high temperature, excessive movement of the goods, tension, torsion, or rough handling during treatment. When silk containing flocons is dyed, these appear as light-coloured spots, which are seen when the fabric is viewed obliquely. They are mistaken sometimes for mildew. They may be formed during weaving or knitting.

**Action of Salts.**—It has been mentioned above that concentrated solutions of many salts dissolve silk. All of these produce damage when only small quantities of them are dried into the silk, and their destructive action is accelerated by exposure to light. Other factors which influence the action are (i) keeping the goods in a warm damp atmosphere, and (ii) the presence of metals which act as catalysts. Salts of weak acids such as sodium acetate do not act in this way. The action of sodium sulphate and sodium chloride is of importance, since they may be present in dyed or weighted silk. Dreaper (*J. Soc. Chem. Ind.*, 1912, 31, 25) suggested the following explanation in the case of sodium chloride:—Firstly it undergoes hydrolysis, thus:



The hydrochloric acid is then oxidized to chlorine, which forms chloramine with the silk protein. It is known that chloramines gradually give off chlorine, which tenders the silk. The sodium hydroxide produced by hydrolysis combines with the carboxyl groups of the protein. Lloyd (*J. Soc. Chem. Ind.*, 1913, 32, 908) described a similar theory to account for the tendering action of sodium sulphate.

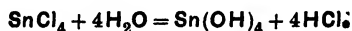
**Weighting of Silk.**—The first process in the dyeing of silk consists of



*degumming*—that is, removing the sericin by *boiling off*. This is accompanied by a loss in weight of from 20 to 25 per cent. Silk is an expensive fibre. When the manufacturer sends one pound of silk to the dyer he will normally receive only 12 or 13 ounces back. In order to replace this loss the goods are often weighted. When the weighting matter introduced is equal to the silk-gum lost the goods are said to be weighted to *par*. Sometimes, however, they are weighted beyond *par* value. If one pound of original raw silk is weighted until it weighs two pounds it is said to be *100 per cent. above par*; or if it weighs four pounds, *300 per cent. above par*. The weighting of silk depends upon its power of adsorbing various metallic salts and organic compounds from their aqueous solutions, these adsorbed bodies being changed subsequently by chemical reactions into insoluble precipitates. These two processes are repeated until the required weight is obtained. The methods used are described in Chapter XXX, but a brief outline may be given here.

When being weighted for blacks, the silk is soaked in a warm solution of tannic acid until adsorption is complete. It is then squeezed, and transferred to a bath containing ferric acetate or basic ferric sulphate. This changes the tannic acid into insoluble iron tannate. The process is then repeated if necessary, each treatment adding about 20 per cent. to the weight.

For light colours the silk is soaked in a cold solution of stannic chloride or of *pink salt*,  $\text{SnCl}_4 \cdot 2\text{NH}_4\text{Cl}$ . It is then washed with water to change the stannic chloride into stannic hydroxide:



After washing and hydro-extracting, the silk is treated with sodium phosphate or sodium silicate in order to produce insoluble tin phosphate or tin silicate. It is then washed thoroughly with water. As before, the operations may be repeated several times if a large amount of weighting is required.

Weighted silk is liable to become tender when kept in a warm atmosphere or exposed to sunlight, if salts such as sodium sulphate or sodium chloride are present.

**Action of Oxidizing Agents.**—Silk is attacked by powerful oxidizing agents such as potassium dichromate, ozone, or chlorine. A five-volume solution of hydrogen peroxide causes a marked fall in the viscosity of a zinc chloride solution.

**Action of Dyestuffs.**—Silk, like wool, has an affinity for acid, basic, and direct dyestuffs, but unlike wool it can be dyed at comparatively low temperatures.

**Wild Silks.**—Silk which is produced by moths of varieties other than *Bombyx mori*—that is, which do not feed on mulberry leaves—is termed *wild silk*. There are many kinds of wild silk, but only a few have commercial value, and these have been to a certain extent cultivated or domesticated. The principal wild silkworms are Asiatic, and the best known, Indian. A Japanese species, *Antheraea yama-mai*, feeds on oak leaves. Another worm, the Eri or Arindi worm, is a native of Assam, and feeds on the leaves of the castor-oil plant. Other varieties, such as *Attacus cynthia*, are cultivated in China. *Attacus atlas*, an Indian variety, produces the largest known moth, the span of its wings reaching to 10 inches, but it produces only a coarse silk. *Antheraea assama*, or Muga silk, is cultivated in Assam. The most important of the wild silks, however, are those known as Tussur silk. There are two species: *Antheraea pernyi* is indigenous to China, and feeds on oak leaves; it is extensively cultivated. *Antheraea mylitta*, the principal species, is found only in India, and is the most important of wild silk-producing worms.

Table XX, given in *Chambers's Encyclopædia*, gives the chief varieties of wild silk, and shows how they compare with the silk of *Bombyx mori*.

TABLE XX.—PROPERTIES OF WILD SILKS.

Name of Worm or Silk.	Country.	Diameter, in.		Tension, or Limit of Stretch before breaking, of Single Fibre 1 Foot long, m.		Strength of Single Fibre, drams avoirdupois.		Dimensions of Cocoon, in.
		Outside of Cocoon.	Inner Part of Cocoon.	Outside of Cocoon.	Inner Part of Cocoon.	Outside of Cocoon.	Inner Part of Cocoon.	
<i>Bombyx mori</i> , or mulberry silk . . . . .	China.	31.50	31.56	1½	1½	2½	2½	1½ × 1½
	Italy.	21.50	31.00	1	1½	2½	2½	1½ × 1½
	Japan.	18.00	16.50	1	1½	2½	2½	1½ × 1½
	Bengal.	20.00	22.00	1½	1½	2½	2½	1½ × 1½
<i>Bombyx textor</i> . . . . .	India.	35.00	25.00	1½	1½	2½	2½	1½ × 1½
<i>Antheræa mylitta</i> , or Tus-sur silk . . . . .	"	7.00	7.00	1	1	7	8	1½ × 7/8
<i>Attacus ricini</i> , or Eria silk . . . . .	"	5.00	14.50	1	1½	1½	2½	1½ × 2
<i>Attacus cyathia</i> , or Ailanthus silk . . . . .	"	12.50	12.50	1	1½	2½	2½	1½ × 2
<i>Antheræa assama</i> , or Muga silk . . . . .	"	14.50	10.50	1	1½	2½	3	1½ × 1
<i>Actias selene</i> . . . . .	"	10.00	11.00	1	1½	2	2½	3 × 1½
<i>Attacus atlas</i> . . . . .	"	18.00	10.00	1	1½	2½	2½	3½ × 7/8
<i>Antheræa yama-mai</i> . . . . .	Japan.	10.00	10.00	1	1	2½	3	1½ × 7/8
<i>Cricula trifenestrata</i> . . . . .	India.	..	8.50	..	..	..	..	2 × 3½

*Tussur Silk*.—The life-history of the Tussur worm is similar to that of *Bombyx mori*. The worm when mature is about 5½ inches in length. It produces a hard, compact cocoon, the silk having a brown or fawn colour. The silk is more difficult to work than that of *Bombyx mori*, chiefly because the thread is not continuous, owing to intermittent spinning by the worm. Hence it is well adapted to the production of chappe or spun silk.

As will be seen from Table XX, Tussur silk is coarse and strong. It differs from ordinary silk also in that the colour is distributed throughout the fibre, and is not confined to the gum. This is the case with most varieties of wild silk. The colour depends upon the nature of the food to a certain extent. Japanese wild silk is generally greenish in colour. Not only is the colour distributed throughout the fibre, but it is very difficult to bleach. Consequently wild silks and particularly Tussur silk are largely used in their natural colour, i.e. unbleached.

The microscopic structure of Tussur silk is distinctly different from that of *Bombyx mori*. The sheath of sericin is difficult to distinguish; the fibre is coarse, and shows marked longitudinal striations with occasional constrictions (Fig. 81). The latter give the silk the appearance of having a natural twist. The cross-section of the fibre is also not circular but irregular in shape.

The chemical properties of Tussur silk are the same as those of true silk, but it is much more resistant to the action of acids, alkalis, and solvents. It

may, in fact, be distinguished from the latter by this property, as will be noted from Table XXI. Tussur silk may be distinguished also from ordinary silk by its action on Millon's reagent: when ordinary silk is treated with Millon's

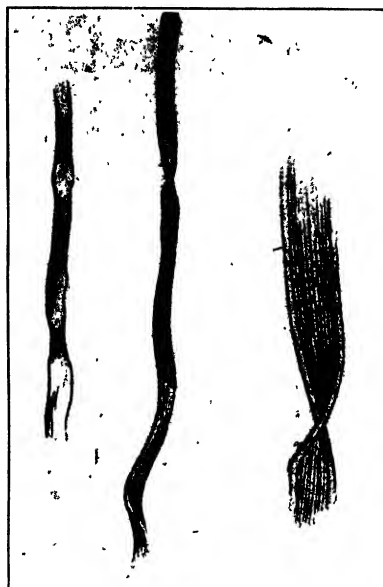


Fig. 81.—Tussur Silk.

reagent it gives a red colour, while with Tussur silk a brown colour is produced. Tussur silk may be estimated in the presence of true silk by taking advantage of its different solubility in hydrochloric acid or dilute sodium hydroxide.

TABLE XXI.—CHEMICAL RESISTANCE OF TRUE AND TUSSUR SILK.

Treatment.	True Silk.	Tussur Silk.
Boiling 1 per cent. sodium hydroxide .	Dissolves rapidly.	Takes from 30 to 50 minutes to dissolve.
Cold hydrochloric acid (sp. gr. 1.16) .	„	Dissolves very slowly.
Zinc chloride solution („ „ 1.67) .	„	Dissolves slowly.

**Spider silk** would be of even greater value as a textile fibre than true silk if it could be obtained in sufficient quantity. A large Madagascar spider, *Nephila madagascariensis*, produces 200 metres per month of a white or orange-yellow, almost transparent silk. Its diameter is less than that of ordinary silk, while its tensile strength and elasticity are as great. The fibre is like that of true silk, composed of ultimate fibrils cemented together. It swells in cold water and decreases in length. It differs from ordinary silk in not having a sheath of gum or sericin.

**Byssus** or **sea silk**, obtained from the beard of a certain shell-fish, also has properties similar to those of silk, but, like spider silk, has no sheath of sericin.

## CHAPTER XIV.

### WOOL AND HAIR.

THESE fibres constitute the protective covering of the mammalian animals, and are growths of the epidermis—that is, consist essentially of the same elements. Horns, nails, and hoofs are of similar origin and are fundamentally the same.

**Structure of the Skin.**—The skin consists of two distinct layers: (i) the epidermis or cuticle, and (ii) the cutis vera or corium. The epidermis is the

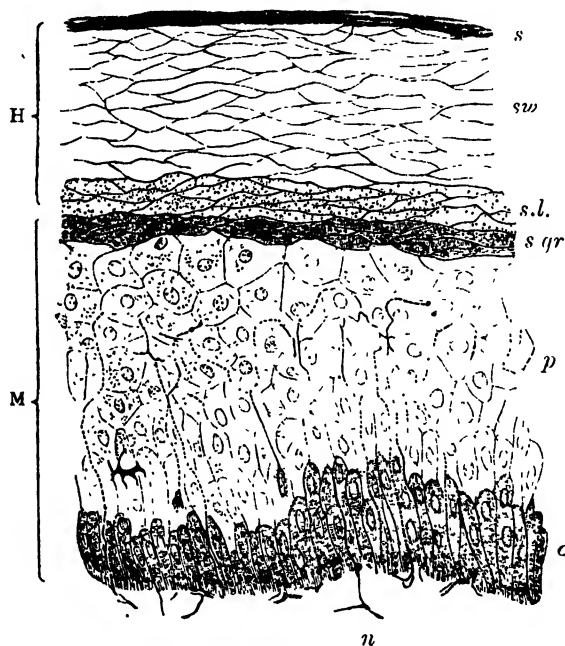


Fig. 82.—Section of Epidermis. (Ranvier.)

*H*, horny layer, consisting of *s*, superficial horny scales; *sw*, swollen-out horny cells; *s.l.*, stratum lucidum; *M*, rete mucosum or Malpighian layer, consisting of *p*, prickle-cells, several rows deep; *c*, elongated cells forming a single stratum near the corium; and *s.gr.*, stratum granulosum of Langerhans, just below the stratum lucidum; *n*, part of a plexus of nerve-fibres in the superficial layer of the cutis vera. From this plexus fine varicose nerve-fibrils may be traced passing up between the epithelium cells of the Malpighian layer.

visible external part, having chiefly protective functions. The cutis vera, or lower layer, is looser in structure. It contains the sweat- and fat-glands, and is well supplied with nerves and blood-vessels. Each of these two layers is subdivided into several distinct portions. Those of the epidermis are shown in Fig. 82.

The hair consists of two parts, viz. the root and the stem or shaft. The root *R* (Fig. 85) is fixed at the base of the follicle. The stem or shaft *S* is approximately cylindrical, tapering to a point at its free end. It grows

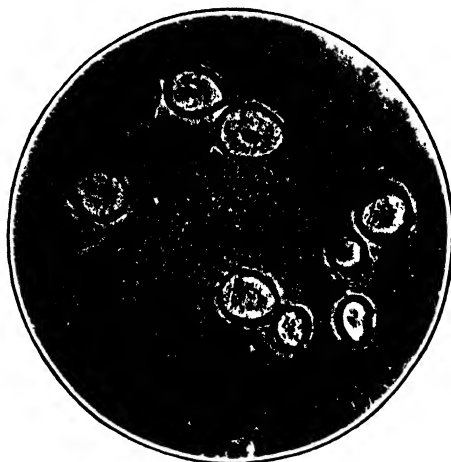


Fig. 86.—Transverse Sections of Wool.

continuously, new cells being formed and pushed up from the root of the follicle.

When a transverse section of a hair (Figs. 86 and 87) is examined under the microscope, it is seen to consist of three distinct parts: On the surface

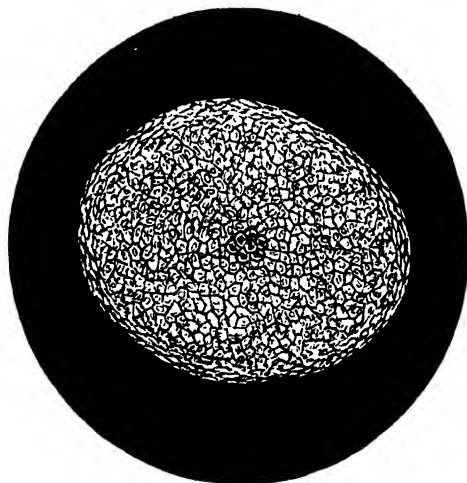


Fig. 87.—Transverse Section of Wool. (Bowman.)

is a layer of flat horny cells or scales, known as the *cuticle* or *epithelium*. Immediately beneath these is a layer of compressed cells, which forms the bulk of the hair, and constitutes the *cortex*. If these cells are teased out they are found to be spindle-shaped, as is seen in Fig. 88. The colour, strength, elas-

ticity, suppleness, and other valuable properties of the fibre are determined chiefly by the cortex. Towards the centre of the fibre the cells of the cortex become gradually less compressed and rounder, till at the centre are found a number of comparatively large rounded cells, which constitute the *medulla*. The medulla is not, however, always visible—that is, sharply distinguished from the cortex. This is generally the case in high-grade wools, the best types being apparently devoid of medulla.

The epithelial scales of a wool fibre are not cemented or fastened to the surface of the fibre throughout their whole length. About one-third of the scale is free from the surface, and points towards the tip of the fibre. Further, the free edge has an irregular or imbricated outline, more or less pointed. The size and shape of these scales vary somewhat with the origin of the wool.

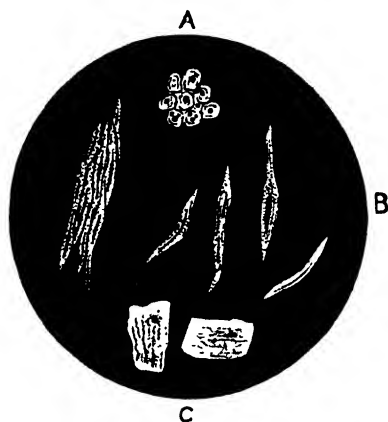


Fig. 88.—Cells constituting Hair.  $\times 300$ .

A, Cells from medulla with nuclei and fat globules.

B, Cells from cortical substance with elongated nuclei and pigment cells.

C, Structureless horny scales from the cuticle. (After Bowman.)

The appearance of the scales is seen in Fig. 89. In English wool the medulla can be seen also showing through the epithelial scales.

**Hair and wool** are essentially the same. They differ only in details, and no hard and fast line can be drawn between them. The following differences may, however, be noted:

In *wool* the edges of the epithelial scales are free. The scales themselves are comparatively large, and the free edges pointed. The medulla is generally indistinct or absent. Wool fibres have often a natural curl, and felt readily when rubbed or boiled with hot soap and water.

In a *typical hair* the epithelial scales (Fig. 90) are generally smaller and more numerous than in the case of wool. Their outline is rounded instead of pointed, and there is no free edge; that is, the scale adheres firmly to the cortex. The medulla is more plainly marked than in wool, though, owing to the prevalence of colour, the fibre may require bleaching before it can be seen. Hair has comparatively little natural curl, and much less felting power than wool.

The comparative differences between wool and hair are illustrated in Fig. 91, which shows a human hair, high-grade mohair, and a typical wool fibre. The free edges of the epithelial scales are purposely rather exaggerated in the wool fibre.

All stages of development from a typical wool to a typical hair may be met with on the same animal, and even in a single fibre. Fig. 92 shows three different portions of the same fibre of sheep wool.

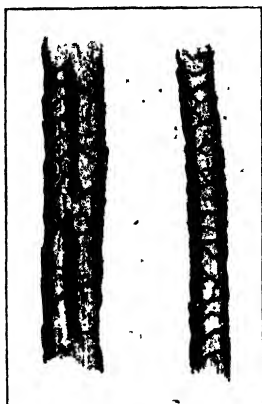


Fig. 89.—Wool Fibres.

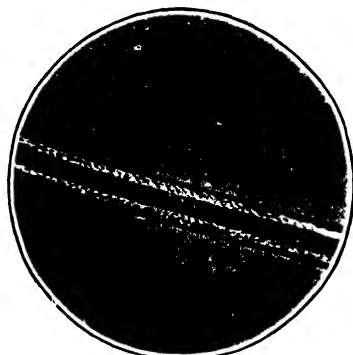
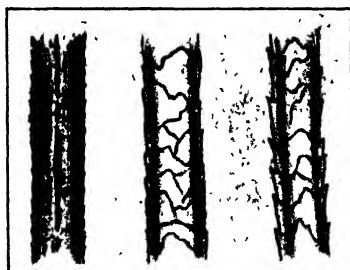


Fig. 90.—Human Hair.

The typical modern wool fibre, with its regularity and apparent absence of medulla, is largely the result of selective breeding, and its permanence depends to a great extent upon the maintenance of the purity of the breed.

Some of the commoner hairs are horse hair, cow hair, camel hair, alpaca, mohair, and cashmere. The last three are obtained from varieties of the



Human hair. Mohair. Wool.

Fig. 91.



Upper. Middle. Lower.

Fig. 92.—Portions of the same Wool Fibre.

goat. Coarse hair like that of the horse and cow has only a limited use. Camel hair is, however, very soft and silky, and is of considerable importance. Owing to the difficulty of bleaching, it is used generally in its natural state, or dyed a dark colour. Fig. 93 shows the microscopic appearance of camel hair.

Amongst the goats allied to alpaca are the llama and vicuna, both of which are native to Chili and Peru. In structure they stand about halfway between typical hair and wool. In the textile trade the terms *alpaca* and *vicuna* have also another meaning, being applied to mixtures of wool and cotton.

Mohair is obtained from the Angora goat of Asia Minor. The fibres are long and silky, and have a high lustre. The epithelial scales are pointed like those of wool, and have free edges. The fibre is, in fact, more closely allied to wool than to hair. Cashmere comes from the Cashmere goat of Tibet. It is a long, soft fibre, used for Indian shawls and other textile materials, and, like mohair, is more nearly a wool than a hair. Mohair and alpaca fibres are illustrated in Figs. 91 and 94.

**Wool-marketing.**—The chief sources of wool used in this country are Australia, New Zealand and S. Africa, together with a small quantity produced in Great Britain. Until the outbreak of war in 1939, wool was sold in England by public auction at the Coleman Street Wool Exchange, London, and in a similar manner in Australia. At the present time (1944) the Govern-

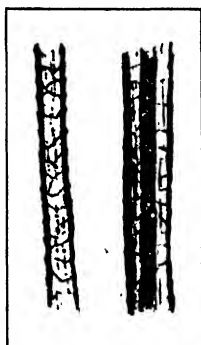


Fig. 93.—Camel Hair.



Mohair. Alpaca.

Fig. 94.

ment handles the selling and distribution of all wool, and it is doubtful whether the old method will be used again.

**Varieties of Wool.**—There are many varieties of true wool, produced by different types of sheep. They differ, chiefly, in length and diameter of fibre, size and number of epithelial scales, felting power, natural curl, softness, lustre, and colour. According to their characteristics they are suitable for different purposes. The highest type of wool is produced by the merino sheep of Spain. Australian and New Zealand wools have been developed by scientific crossing of the merino with other sheep. These crossbred wools, such as *Botany*, are the best that we have, and are characterized by great regularity of structure and number of scales or serrations. The fineness of diameter varies inversely with the length of the fibre. These together determine the spinning and also to a considerable extent the felting power.

Among the other common varieties of wool the following may be mentioned: *Southdown* has a fine fibre with a low felting power, and is, therefore, suitable for flannels. *Lincoln* and *Leicester* wool is comparatively coarse, but has a high lustre, and is used for dress fabrics. The *Cheviot* sheep produces a short, strong, coarse fibre with a high felting power, which makes it useful for the production of Cheviot cloths. Merino and crossbred wools are characterized by regularity of length of fibre and fineness, and are used for the best kinds of woollen fabrics. Table XXII summarizes the extremes of physical properties met with in different types of wool.



TABLE XXII.—CHARACTERISTICS OF TYPICAL VARIETIES OF WOOL.

Coarse: Lincoln and Leicester.	Medium: Southdown, Oxford.	Fine: Botany, Merino.
Lustrous, strong, and straight. Serrations 600 to 1000 per inch. Scales horny and firmly attached.	Halfway between coarse and fine.	Non-lustrous, soft, curly, and fine. Serrations from 2800 to 5000 per inch. Scales funnel-shaped, and overlap clearly. Free edges marked and serrated.
Length, 5 to 8 inches.	Length, 3 to 8 inches.	Length, 2 to 5 inches.

F. H. Bowman, in his work on the *Structure of the Wool Fibre*, p. 221, gives the following relative strengths of different kinds of wool fibres, taking that of the Southdown sheep as 100:

Southdown . . . . .	100	Cheviot . . . . .	75
Australian merino . . . . .	85	Leicester . . . . .	72
Oxford Down . . . . .	82	Lincoln . . . . .	68
Shropshire . . . . .	78	Cotswold . . . . .	64

Table XXIII, from Hannan's *Textiles Fibres of Commerce*, gives the relative tensile strength, elasticity, and diameter of different hairs and wools.

TABLE XXIII.—PHYSICAL PROPERTIES OF HAIRS AND WOOLS.

Fibre.	Breaking Strain, grains.	Elasticity, percentage of length.	Diameter of Fibre before breaking, in.	Diameter of Fibre after breaking, in.	Difference, in.
Human hair . . . . .	1680 1720	0.374 0.371	0.00342 0.00342	0.00283 0.00283	0.00059 0.00059
Lincoln wool . . . . .	580 465	0.240 0.270	0.00185 0.00185	0.00161 0.00150	0.00024 0.00015
Leicester wool . . . . .	480 510	0.240 0.270	0.00175 0.00158	0.00131 0.00138	0.00044 0.00020
Northumberland wool . . . . .	420 440	0.224 0.300	0.00143 0.00155	0.00120 0.00132	0.00023 0.00023
Southdown wool . . . . .	82 80	0.230 0.210	0.00101 0.00097	0.00080 0.00082	0.00011 0.00015
Australian merino . . . . .	48 46	0.387 0.251	0.000540 0.000472	0.000354 0.000361	0.000186 0.000111
Saxony merino . . . . .	43 37	0.321 0.263	0.000317 0.000331	0.000210 0.000213	0.000107 0.000118
Mohair . . . . .	600 590	0.285 0.306	0.00174 0.00180	0.00132 0.00142	0.00042 0.00038
Alpaca . . . . .	150 138	0.231 0.220	0.000521 0.000511	0.000387 0.000402	0.000134 0.000109

Among the characteristics of good wool are, according to Bowman—

- (1) Uniformity of length and fineness of fibre.
- (2) Suppleness, elasticity, and uniformity of tensile strength.
- (3) Absence of hard or brittle fibres.
- (4) For the class of wool, the scales must be as numerous as possible, of uniform size, and closely adherent to the surface so as to prevent felting in the fleece or the accumulation of dirt under the free margins.



[From Hannan's *Textile Fibres*.

Fig. 95.—Woollen Yarn.

- (5) Good colour and high lustre.

- (6) Soft feel and resilience.

Wool may, in general, be classified as long and short staple. *Long-staple wools* include those whose fibres are above  $1\frac{1}{2}$  inches in length. Among these are Lincoln, Leicester, and Botany wools.

They are suitable for the spinning of worsted yarns, which are used in the manufacture of fabrics where strength must be due to natural tensile strength of the fibre rather than acquired by felting.

*Short-staple wool* includes fibres of  $1\frac{1}{2}$  inches and less. It is used chiefly in the manufacture of woollen as opposed to worsted yarns. Worsted yarns are spun like cotton—that is, the fibres are laid parallel to one another and twisted together round a common longitudinal axis. In woollen yarns, on the other hand, the fibres are not necessarily parallel. They are in fact twisted together in such a way that many of them are in different directions entangled with one another. Thus, the yarn does not derive its tensile strength entirely from the length of the fibre and the twist, but from the mechanical interlocking of the entangled fibres. This also makes it possible to felt cloth made from the yarn much more completely than that made from a worsted. Hence, where a solid, highly felted fabric is required, woollen yarns are suitable.



Fig. 96.—Worsted Yarn.

The difference between a woollen and a worsted yarn is shown by Figs. 95 and 96.

These two kinds of yarns are numbered on different systems. For worsted yarns the hank is 560 yards, and the count is the number of hanks required to make one pound. In the case of woollen yarns the hank is

256 yards, or they are numbered sometimes by the number of yards to the ounce.

**Bradford Classification of Wools.**—In Bradford wool is divided broadly into (1) merino, (2) crossbred, and (3) low wool. It is further subdivided into (a) combing wool for worsteds, and (b) clothing wool for woollen yarns. These in turn are classified into different qualities represented by numbers, viz.:

Merino.	Crossbred.
80's quality.	58's quality
70's    "	56's    "
64's    "	50's    "
60's    "	48's    "
	46's    "
	44's    "
	40's    "
	36's    "
	32's    "

No sheep produces exclusively long or short fibres, but a mixture of both. A healthy, well-bred sheep tends to give fibres of uniform length over certain areas of its body, but the average length of staple varies with the part of the fleece from which it is taken.

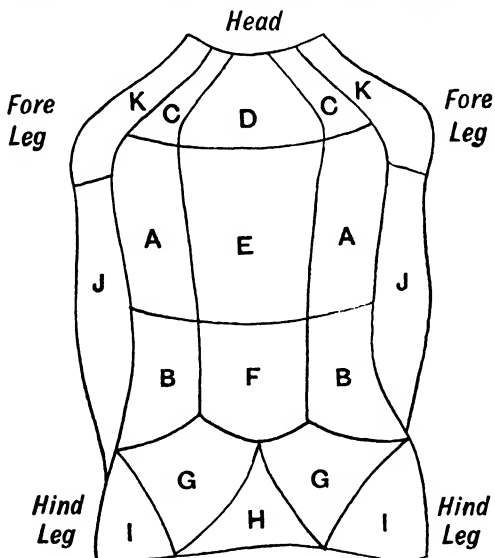


Fig. 97.—Grades of Wool in Spread Fleece.

ent qualities of fibre obtained from it are indicated by the letters, *A* indicating the highest grade.

In connection with wool-sorting, mention may be made of *anthrax*, or *wool-sorter's disease*. This is caused by the presence in the wool of either the anthrax bacillus or its spores. These generally gain entrance into the human body through a cut or abrasion which is unprotected. The disease is very fatal to both human beings and animals. All hair and wool, particularly that from foreign countries where little trouble is taken to stamp out the

Hence, wool is subjected to a process of carding or combing designed to separate the long from the short fibres, this being preceded by a preliminary process of hand sorting. The longer fibres obtained by combing are termed *tops*, and the shorter *noils*. Tops are used for spinning fine counts and worsted yarns or warps. From noils, woollen yarns or wefts are obtained. For different purposes blends of long and short fibres may be used, or of the wool from different varieties of sheep.

**Wool-sorting.**—After shearing, the fleece is spread out and sorted by a wool-sorter into its various grades. Fig. 97, given by Bowman, shows the spread fleece of a Leicester sheep. The differ-

disease, is liable to contain anthrax germs. They have been found, for example, in imported shaving-brushes.

Wool may be obtained from either live or dead sheep. That shorn from the living sheep is called *fleece* wool, while when removed from the dead animal it is known as *skin* wool. Fleece wool is of two kinds: the first time the sheep is shorn the product is *lamb* or *hog* wool, while subsequent shearings give *wether* wool. Hog wool is finer in texture than wether wool, and has the pointed upper ends of the original fibre. Wether wool, on the other hand, has blunt ends.

When the sheep dies or is killed, its skin, together with the wool, is soaked in milk of lime or other depilatory agent to loosen the hair roots. The wool is then pulled out, and constitutes skin wool. Skin wool is somewhat harsh owing to the action of the alkali on the wool substance. The epithelial scales are also frequently damaged.

**Abnormal Fibres.**—These are found occasionally in all kinds of wool. The number present depends largely upon the breed of sheep, care being taken in breeding only from good animals and ensuring suitable environment and food and freedom from disease. If care is not exercised there is a gradual reversion to type, accompanied by a deterioration of fibre or an excessive number of abnormal ones.

The chief kinds of abnormal fibres met with are—

(1) *Cots*.—These consist of little masses or knots of tangled and felted hairs. They are caused by deficiency of natural wool-fat, which serves to lubricate the fibres. Constant rubbing on the part of the sheep to relieve itching, or lying in muddy fields exposed to rain, also tends to produce cots. If they are not removed during the carding process they cause trouble in spinning.

(2) *Kemps*.—These are, perhaps, the most troublesome kind of abnormal fibres. They are due to the coalescing of the epithelial scales to form opaque, ivory-like rings, which sometimes extend for a considerable length. The change is often carried beyond the scales into the cortex, giving a hard, horny fibre apparently without structure. Moreover, two or more adjacent fibres may coalesce to form a *compound* or *flat* kemp.

Kemps are more common on the neck and legs than on other parts, and are found more frequently in diseased than in healthy sheep. Their occurrence is stamped out as far as possible by never breeding from sheep which have a tendency to produce them.

In the variety known as *flat kemps* the cortex and medulla remain distinctly visible, the transformation to kempy substance being limited to the epithelial scales. The appearance of kemps under the microscope is seen in Fig. 98. Priestman (*J. Soc. Dyers Col.*, 1915, 31, 5-8) says that in kemps the medulla is composed of approximately spherical cells, which, through some peculiarity of growth, take the place of the spindle-shaped cells of normal wool fibre. These spherical cells occupy the same volume as the normal medullary cells, making the kemp fibre about one-fourth of the length and twice the diameter of the normal fibre. The opacity is an optical effect of refraction, and the kemp becomes transparent when saturated with benzene. Flat kemps owe their lustre and opacity to the fact that they are flat, hollow

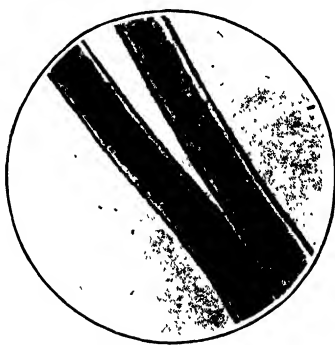


Fig. 98.—Kemps.

tubes. It is uncertain whether the internal cells are absent, but, if present, they are entirely modified, sometimes contracting and leaving a hollow air-space.

Kemps in wool are objectionable chiefly for two reasons: In the first place, owing to the absence of the free edges of the scales the fibres cannot be locked together properly in spinning, and hence the yarn is deficient in tensile strength. Secondly, they are practically impervious to water and dye liquors. Kemps can be wetted down only by boiling with water, and, owing to their impenetrability, they do not take up dyestuffs. Kempy wool, as a rule, gives uneven or patchy results in dyeing.

More recent work by Duerden and Ritchie (*Union of South Africa Science Bulletin*, No. 34) shows that a kemp is a straight, coarse, opaque, white fibre having a thick central medulla with hollow interspaces containing inclusions of air. Wool has no medulla and no air inclusions.

(3) *Hypertrophy* or *Atrophy* is sometimes found in diseased, badly fed, or low-bred sheep. A fibre which gradually or suddenly increases in diameter



Fig. 99.—Atrophy and Hypertrophy.



Fig. 100.—Diseased Fibres.

is said to be hypertrophied. Similarly, atrophy denotes a sudden variation in the other direction—that is, from normal to subnormal diameter. These are seen in Fig. 99.

(4) *Diseased fibres* are indicated generally by the partial or complete destruction of the epithelial scales, exposing the underlying cortex. Such damage may be caused by parasites or organic disease. Destruction of the wool fibre by parasites is prevented by the use of antiseptic sheep-dips. But it must be remembered that destruction of the epithelial scales is the common sign of all kinds of damage, such as that due to acids, alkalis, moulds, or putrefactive organisms. Fig. 100 shows the appearance of damaged fibres under the microscope.

**Definitions.**—In dealing with woollen materials there are certain definitions which are important, viz.:

*Merino.*—(1) Wool from the merino sheep; (2) yarn spun from a mixture of wool and cotton (e.g. 85 per cent. cotton and 15 per cent. wool); (3) cotton fibre with a raised nap.

*Shoddy* consists of short fibres from clippings of old clothes, etc. about 1 inch in length. The ends of such fibres are generally frayed, and the

scales frequently absent. Shoddy may consist of a mixture of wool and cotton.

*Mungo* is similar to shoddy, but is made from shorter fibres,  $\frac{1}{4}$  to  $\frac{3}{4}$  inch. It is generally made from wool-rags.

*Extract* is similar, but is made from wool and cotton waste by carbonizing and removing the cotton.

*Alpaca* (or *Vicuna*).—These terms not only indicate the hair of the respective goats, but also long-staple waste with or without cotton.

### Composition of Raw Wool.

Raw wool consists of (1) keratin, or wool-substance; (2) wool-fat; (3) suint, or dried perspiration; (4) dirt; (5) mineral matter; (6) water; and (7) burrs, or vegetable matter.

The proportions in which these bodies are present is variable, a sample of raw wool yielding from 30 to 70 per cent. of wool according to its conditions of growth. The approximate composition of dry wool may be taken as

Wool . . . . .	33 per cent.	Fat . . . . .	12 per cent.
Dirt . . . . .	26 „	Mineral matter . . . . .	1 „
Suint . . . . .	28 „		

**Suint** is a very complex mixture. It contains potassium salts of fatty acids, such as oleic and stearic, and also potassium carbonate. Simpler organic acids, such as acetic, lactic, butyric, valeric, and caproic acids, are also present, both in the free state and as potassium salts. The amino acids leucine, glycine, and tyrosine have also been identified. These bodies are all soluble in water, and can be removed from wool by washing. They are extracted in this way, and are used as a source of potash.

**Wool-fat** differs from ordinary fats. It is not a glyceride, but a compound of fatty acids with cholesterol,  $C_{27}H_{45}OH$ , and its isomer ischolesterol. But it contains also uncombined cholesterol and ischolesterol, and some free fatty acids. The term *wool-wax* is used sometimes to denote the true wool-grease, i.e. that portion in which the fatty acids are in a state of combination with the cholesterol. This is a yellowish waxy substance soluble in organic solvents. Like other waxes it is difficult to saponify, but when heated for a long time with alcoholic potassium hydroxide, or for shorter periods with potassium hydroxide and glycerin, it is decomposed, giving cholesterol and the potassium salt of the fatty acid. It has the power of absorbing large quantities of water, forming permanent emulsions. It can be mixed with about 80 per cent. of water and still retain a creamy consistency. *Lanoline* consists of a mixture of wool-wax with about 25 per cent. of water. The chemical composition of wool-fat is still uncertain.

According to Lewkowitz, ordinary fatty acids, such as stearic, palmitic, or oleic, are not present, but he proved the presence of hydroxy acids, which contain both hydroxyl ( $-OH$ ) and carboxyl ( $-COOH$ ) groups.

**The natural mineral matter** rarely exceeds 1.5 per cent. Its composition appears to vary somewhat with the soil on which the sheep graze. Bowman gives the following analysis of ash in percentages:—

Potash, $K_2O$ . . . . .	31.1	Silica . . . . .	5.8
Soda, $Na_2O$ . . . . .	8.1	Sulphur trioxide . . . . .	20.5
Lime . . . . .	16.0	Phosphorus pentoxide . . . . .	Trace
Alumina and iron oxide . . . . .	12.3	Chlorine . . . . .	Trace

**Dirt** is, of course, entirely adventitious. It is cemented to the fibre by means of grease, and is removed with the latter during the scouring process.

**Burrs**, or vegetable fragments, are commonly due to the sheep scratching against bushes to relieve itching. They are removed from the scoured wool by a process termed *carbonization*, which will be described later. Fig. 101 shows the appearance of burrs in scoured wool.

**Wool-substance.**—This consists chiefly of a nitrogenous body called *keratin*, which is closely allied to the proteins. The presence of a small quantity (1.68 per cent.) of another nitrogenous compound, termed *wool-gelatin*, has been recorded also. Keratin may be prepared from wool in the following way:

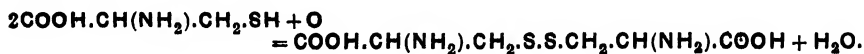
(i) Dry wool is extracted in a Soxhlet or continuous-extraction apparatus



Fig. 101.—Burrs.

with ether to remove the oil and fat, and then with hot alcohol to dissolve out the soaps; (ii) the residue is then dried, and extracted with warm distilled water to remove suint; (iii) the washed residue is soaked in a 1 per cent. solution of hydrochloric acid to decompose any calcium or magnesium soaps which may be present. After washing with distilled water, it is dried, and then extracted again with ether to dissolve the liberated fatty acids. The extracted residue is washed with very dilute ammonia, then with hot distilled water till free from alkali, and finally dried.

**Nature and Properties of Keratin.**—Wool-protein or keratin differs from other proteins in containing a considerable proportion of sulphur, varying from 3.10 to 4.00 per cent. according to the origin of the wool. This sulphur is due to the presence of cystine,  $\text{COOH.CH(NH}_2\text{).CH}_2\text{.S.S.CH}_2\text{.CH(NH}_2\text{).COOH}$ . A high sulphur content indicates a more stable type of keratin than a low sulphur content, offering greater resistance to processing and decay. This cystine is probably formed from cysteine, which is present in the blood, by a process of oxidation, thus:

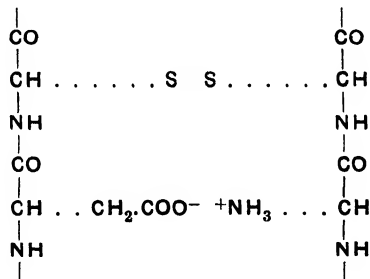


The percentage of nitrogen in keratin is about 17.0, but varies somewhat with the quality of the wool.

When wool is hydrolysed, it yields a mixture of amino acids which, in addition to cystine, include

Aspartic acid . . . . .	$\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{COOH}$
Glutamic acid . . . . .	$\text{COOH} \cdot (\text{CH}_2)_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{COOH}$
Arginine . . . . .	$\text{NH} \cdot \text{C}(\text{NH}_2) \cdot \text{NH} \cdot (\text{CH}_2)_3 \cdot \text{CH}(\text{NH}_2) \cdot \text{COOH}$
Lysine . . . . .	$\text{NH}_2 \cdot \text{CH}_2 \cdot (\text{CH}_2)_3 \cdot \text{CH}(\text{NH}_2) \cdot \text{COOH}$
Histidine . . . . .	$\begin{array}{c} \text{N} - \text{CH} \\ \parallel \\ \text{CH} \cdot \text{NH} \end{array} > \text{C} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{COOH}$

The diamino acids and histidine account for the basic nature of wool, whilst aspartic acid and glutamic acid combine with alkalis. Cystine, which is characteristic of keratin, is decomposed easily. When heated to  $150^\circ \text{C}$ . it gives sulphuretted hydrogen; with alkalis sodium sulphide is formed; whilst oxidizing agents convert some of its sulphur into sulphuric acid. It is probable (Trotman and Sutton, *J. Soc. Chem. Ind.*, 1926, **45**, 10T) that two distinct proteins are present in wool, which contain different proportions of sulphur, viz. 4.05 and 1.49 per cent. respectively, and different amounts of diamino nitrogen. According to Speakman and Hirst (*Trans. Farad. Soc.*, 1933, **29**, 148) wool protein is composed of long peptide chains, bridged by cystine and salt linkages, and running parallel to the length of the fibre, in the following manner:—



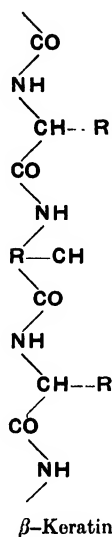
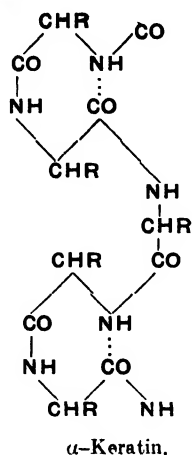
Astbury (*J. Soc. Dyers Col.*, 1933, **49**, 168) showed, by X-ray analysis, that the peptide chains are regular repetitions of the unit  $-\text{CO}-\text{CH}-\text{NH}-$ , and that

they carry side-chains varying in character according to the nature of the amino acid from which they are derived. Astbury has shown further that the long peptide chains are coiled in the manner illustrated on p. 168 where R indicates a side-chain. These coiled chains (termed  $\alpha$ -keratin) can be pulled out straight ( $\beta$ -keratin), and return to  $\alpha$ -keratin when the tension is released, thus accounting for the elasticity of the fibre.

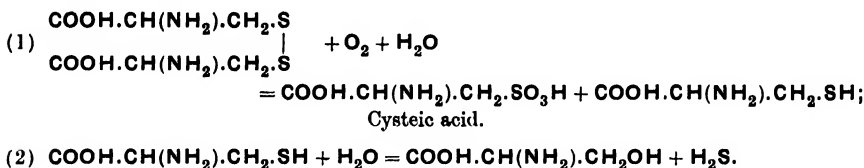
**Cystine.**—The chemistry of wool is closely associated with that of cystine, and a brief account of this may be given here. Cystine may be prepared from wool by the method of Folin: 100 g. of purified wool is refluxed with 200 ml. of concentrated hydrochloric acid for 6 to 7 hours, the mixture being kept just boiling. It is then cooled and filtered, and sodium acetate is added to the filtrate until no change takes place with congo-red paper. The filtrate is allowed to stand for 24 hours, after which the precipitate is collected, washed with water, and dried at  $110^\circ \text{C}$ . The product should give no reaction with Millon's reagent (absence of tyrosine). It may be purified by dissolving it



in hydrochloric acid, decolorizing with charcoal, neutralizing with sodium acetate, and allowing it to crystallize.



Cystine forms colourless hexagonal plates or prisms containing 26.69 per cent. of sulphur, which are typical when crystallized from ammonia. It is insoluble in water, alcohol, or ether, but is soluble in dilute acids and alkalis. The solution in sodium hydroxide contains sodium sulphide. Cystine is readily decomposed, giving cysteine,  $\text{COOH} \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{SH}$ . When exposed to damp air, it yields cysteine and cysteic acid. The cysteine is then hydrolysed with the formation of sulphuretted hydrogen:



Cysteic acid is oxidized gradually at ordinary temperatures to taurine,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$ , and carbon dioxide; whilst at temperatures above  $100^\circ \text{C}$ . it yields sulphuric acid, carbon dioxide, taurine, and alanine,  $\text{CH}_3 \cdot \text{CH}(\text{NH}_2) \cdot \text{COOH}$ . When oxidized with iodine, cysteine gives cystine with elimination of water.

The cystine content of wool does not correspond to the total sulphur, and Morner (*J. Soc. Chem. Ind.*, 1915, **34**, 446) states that when wool is oxidized with nitric acid methylsulphonic acid is formed, which is not given by cystine. He concludes, therefore, that wool must contain sulphur in some other state of combination. It may be noted, however, that sulphuretted hydrogen is given off when wool is heated with hydrochloric acid.

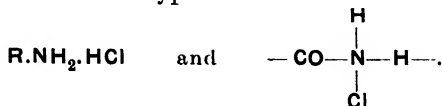
### Properties of Wool.

**General Properties.**—Wool is an amphoteric colloid. Its iso-electric point according to Speakman is pH 4.7 to 4.8; Elöd gives pH 4.9, whilst Harris

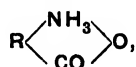
found it to be 3.4. It is possible that there are two iso-electric regions. The following are some of the methods which have been used in the determination:

- (1)  $pH$  at which swelling power is a minimum.
- (2)  $pH$  at which the rate of migration of small particles in an electric field is least.
- (3)  $pH$  at which combination with the radical  $Fe(CN)_6$  begins.

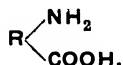
Like all proteins, wool has both acid and basic properties. In the presence of acids it forms compounds of the types



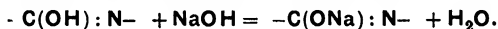
At the iso-electric point it assumes the form—



changing when treated with water to



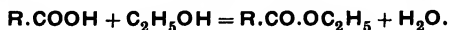
When treated with an alkali the carboxyl groups are neutralized, giving  $R.COONa$ ; the  $-CO-NH-$  groups then change from the keto to the enol form,  $-C(OH):N-$ , the latter reacting with alkalis thus:



The basic properties of wool are very marked, whilst the acid properties are weaker. It is more difficult to remove acid from wool by washing with water than alkali. When treated with nitrous acid, wool undergoes diazotization, the primary amino groups being replaced by hydroxyl groups in accordance with the equation:



When wool is heated with an alcohol in the presence of a condensing agent such as sulphuric acid, the carboxyl groups react to form an ester, thus:



The esterified wool has a decreased affinity for basic dyestuffs, whilst deaminated wool has a lower affinity for acid dyestuffs. Unlike silk, wool cannot be dissolved without decomposition.

Wool is very hygroscopic, and can take up a large quantity of moisture without feeling wet. Wright (*J. Soc. Chem. Ind.*, 1909, **28**, 1020) found that (i) the amount of moisture which wool can absorb from the atmosphere depends upon the relative humidity of the air and the purity of the wool; pure wool can absorb from 18 to 20 per cent., but this is not sufficient to account for all the water absorbed by dry normal wool fibre; (ii) natural wool-fat can take up 17 per cent. of its weight of atmospheric moisture; (iii) suint is extremely hygroscopic, absorbing up to 67 per cent. of its weight of water; (iv) fatty matter, other than wool-fat, has a retarding effect on the absorption of water. From these experiments it appears that the amount of water which wool can take up from the atmosphere depends very largely upon its freedom from suint. The normal regain for scoured wool is 18.25

per cent., but for other forms it is different. The following are the regains commonly allowed:—

Wools and waste . . . . .	16	per cent.
Tops with oil . . . . .	19	„
Tops without oil . . . . .	18.25	„
Noils with oil . . . . .	14	„
Noils (scoured or carbonized) . . . . .	16	„
Worsted yarns . . . . .	18.25	„
Worsted and woollen cloth . . . . .	16	„

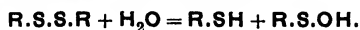
The effect of moisture upon the tensile strength of wool is the opposite to its effect upon cotton, that is, increasing the moisture decreases the strength, and vice-versa. The elasticity, on the other hand, increases with the humidity. Hardy (*J. Soc. Chem. Ind.*, 1920, **39**, 481A) found that when the humidity is increased above 80 per cent. a slight increase of tensile strength is observed. Elasticity increases with the humidity up to 80 per cent., and decreases from 80 per cent. to the saturation-point. Although very hygroscopic, wool wets down slowly at ordinary temperatures, and it is not until a temperature of 140° F. (60° C.) is reached that it takes up water at all rapidly. This is of importance in dyeing, and is the reason why wool is always wetted down with water at 140° F. before dyeing, and generally entered into the dye-bath at this temperature. Kempy wool is still more resistant to wetting. Capillarizing agents such as Turkey-red oil are frequently used to assist the penetration of dye and other liquors. The humidity of the atmosphere is an important factor in the spinning of wool. Dry wool is easily electrified by friction. To prevent this a certain amount of moisture must be present in the fibre and the atmosphere for spinning. A humidity of 50 per cent. is generally necessary. In weaving or knitting yarns into fabrics a lather of soap and neatsfoot oil is used for a similar purpose.

Wool has great elasticity and resiliency. Its tensile strength is intermediate between those of cotton and silk. Animal fibres are generally stronger than vegetable fibres of the same diameter, wool being at least 25 per cent. stronger than cotton. The following table gives the tensile strengths of wool and other fibres in grams per square millimetre:—

Cotton . . . . .	30	Silk . . . . .	45
Flax . . . . .	30	Hemp . . . . .	45
Wool . . . . .	40		

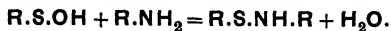
Wool has the power of absorbing gases. It will take up and retain large quantities of such gases as sulphur dioxide and sulphuretted hydrogen.

**Felting of Wool.**—When soaked in hot water, wool gradually swells, and ultimately becomes soft and plastic. In this state it can be pressed or moulded into any desired shape, and, if cooled quickly, retains the new form more or less permanently. According to Speakman, the permanent set acquired by strained animal fibres in steam is due to two consecutive reactions. Internal stress is first dissipated by rearrangement of salt linkages, and hydrolysis of the cystine linkages according to the equation:



With the cystine linkages hydrolysed the fibres can collapse, when released in steam, to a length less than the original length. Such collapse is prevented by prolonged steaming, which leads to the rebuilding of new linkages between the peptide chains by interaction between the free amino groups of arginine and

lysine side-chains, and the products of hydrolysis of the cystine linkage. Since the new linkages resist the action of boiling water, boiling 0.1N. acid and alkali, and boiling sodium bisulphite solution, they are doubtless formed according to the equation:



In general, the setting process is assisted by reagents which facilitate breakdown of the cystine linkage without hydrolysis of the peptide chain, and which give decomposition products capable of condensation with amino groups. Among suitable reagents are solutions of sodium sulphite, sodium bisulphite, and borax at pH 9.2. This property is the basis of some of the finishing processes for woollen garments.

Prolonged boiling with water, especially in the presence of soap or small quantities of alkali, causes wool to shrink and felt. The felting is assisted by rubbing or pressing the material so as to bring the fibres into contact with one another. This property is made use of in the fulling and milling of cloth. The extent of the shrinkage or felting depends upon the variety of wool, some kinds having these properties to a much greater degree than others. The felting of wool has been attributed to different causes. It was originally thought that it was due to the interlocking of the free edges of the epithelial scales. Undoubtedly this has much to do with it, because any treatment which attacks these free edges reduces the felting power of the wool. But, on the other hand, some wools, in which the free edges are very well marked, have not so great a felting power as others where the edges are not so distinct. Another suggestion was that felting is due to the presence in wool of an adhesive gum which softens under the influence of hot soap and water, and glues the fibres together. A still later theory is that advanced by Justin Mueller, who holds that felting is really an attribute of the colloidal nature of wool. When heated in water the fibre swells up like other colloids, becoming changed into a colloidal gel, in which condition the fibres coalesce or felt by mechanical action. The point is difficult to decide, but one thing is quite certain, namely, that any process which destroys the free edges of the epithelial scales, or the scales themselves, reduces the shrinking and felting proportionally to the amount of such destruction. Commercial processes for rendering wool unshrinkable, which will be described later, are founded upon this fact.

**Action of Air on Wool.**—If clean and dry, wool is fairly durable, but it gradually deteriorates when exposed to air. This process is known as *weathering*. This action is accompanied by a gradual destruction of the nap, hardening of the fibre, and loss of its woolly nature. In the case of undyed goods a brownish colour also is produced, as well as a somewhat increased affinity for dyes. In dealing with the action of air on textile fabrics the following factors must be considered: (i) oxygen, nitrogen, and carbon dioxide; (ii) moisture; (iii) hydrogen peroxide and ozone; (iv) light; and (v) micro-organisms. Kertesz (*J. Soc. Chem. Ind.*, 1919, **38**, 496A) investigated the effects of moisture, ozone, and actinic light, investigating each separately. He found that undyed is more rapidly attacked than dyed wool, soft goods more quickly than hard. Materials finished with oil are more resistant than those which are oil-free. He found that, while ozone causes the tendering of wool, it does not produce the peculiar hardening and loss of woolly nature which is so characteristic of weathering. Moreover, certain agents which are supposed to protect wool against weathering had no action in the case of ozone. Moisture did not affect the result. But he could produce all the effects commonly associated with weathering by exposing the wool to the

light from a quartz mercury-vapour lamp, and he concluded, therefore, that actinic light is the chief factor concerned. The action of ozonized air in the presence of light and moisture was investigated by Trotman and Langsdale (*J. Soc. Chem. Ind.*, 1923, 42, 13r), who found that the epithelial scales were gradually destroyed, this action being accompanied by an increased solubility of the wool in dilute acids and alkalis, an increased affinity for acid and basic dyestuffs, a decreased felting power, and, after the action of the ozone had been continued for some time, decreased elasticity and tensile strength. Weathering is accompanied by a change in the composition of the wool-substance. This is indicated by the brown discoloration and the greater solubility. Moreover, wool which has been exposed to air for some time becomes more susceptible to other kinds of damage, such as that produced by acids or alkalis. If ordinary wool be soaked in a cold dilute (1 per cent.) solution of sodium carbonate for about three hours, and the solution tested for soluble proteins by the biuret reaction, very little colour is obtained. But weathered wool gives a strong reaction when treated in this way. This must indicate that some action such as oxidation or hydrolysis has taken place, which has changed the keratin into more soluble compounds. Oxidation might explain the brownish tint produced by weathering. If wool is diazotized with sodium nitrite and hydrochloric acid, and then, after washing, boiled with water containing a little acetic acid, it becomes *de-aminated*, i.e. the original amino groups are replaced by hydroxyl (-OH) groups. This change is accompanied by the production of a brown colour. When this de-aminated wool is treated with diazotized sulphanilic acid a fast yellowish-brown is obtained, while ordinary wool gives much less colour. This indicates an increase in the number of hydroxyl groups present. Whitaker (*J. Soc. Chem. Ind.*, 1914, 33, 479) has suggested that this is what happens when wool is damaged by weathering.

The action of ozone described appears to confirm this view. Further, powerful oxidizing agents, such as persulphates, produce similar results to weathering, and they are known to replace  $\text{NH}_2$ - by OH-groups. When wool is treated with a warm solution of potassium or ammonium persulphate, it becomes gradually yellowish-brown in colour. It then breaks down rapidly when rubbed or boiled with soap and water, and has all the appearances of badly weathered wool.

Fort and Lloyd (*J. Soc. Chem. Ind.*, 1914, 33, 306), however, arrived at a contrary conclusion, namely, that this browning is due to the development of free amino groups, using the potassium salt of naphthaquinone-4-sulphonic acid as a reagent for free amino groups. For example, if undamaged wool is boiled with this



Fig. 102.—Wool damaged by *B. subtilis*.

reagent, it gives only a faint brown colour, but after prolonged weathering a much deeper shade is produced. It may be mentioned that Fort (*J. Soc. Chem. Ind.*, 1916, 35, 833) found that boiling wool with a 5 per cent. solution of sulphuric acid before exposure to air inhibited browning, while the colour of already browned goods was also improved.

The action of micro-organisms, such as moulds and bacteria, is another important factor in the weathering of wool. The action of *Bacillus subtilis* was studied by Trotman and Langsdale (*J. Soc. Chem. Ind.*, 1924, 43, 190r). If wool is infected with a culture of this bacillus, and incubated at a temperature of 37·5° C. for about forty-eight hours, or for a longer time at ordinary atmospheric temperature, effects similar to those of weathering are produced, except that the colour is not affected. With more prolonged action the outline of the epithelial scales becomes faint, and finally disappears altogether, exposing the cortex to view. The same effect is produced by proteolytic enzymes. If the action of the bacillus is prolonged for three or four days the fabric becomes tender, and is easily broken. Microscopic examination at this stage shows that the cortical cells have been liberated and the fibre has become completely disorganized. This is seen in Fig. 102.

Various methods have been proposed to protect wool against atmospheric decomposition. These include treating it with small quantities of salts of chromium and aluminium, aldehydes, such as formaldehyde, tannic acid, or, as suggested by Fort, boiling it with dilute sulphuric acid. As an example, the following patent process of Meister, Lucius, and Brünig is interesting. Wool is treated at the ordinary temperature with salts of chromium or aluminium, particularly with the substances which are used in chrome tanning, such as chrome alum, chromium chloride, and their basic salts. Alum or aluminium sulphate in the form of neutral or basic salts may also be employed. The treatment of the wool may take place by prolonged steeping or

by padding or impregnating with more concentrated solutions, and may be carried out either on the loose wool or on piece-goods. The treated wool possesses increased resistance to the action of air and light. It must be said that opinions differ considerably as to the protective action of these processes.

**Detection of Damage.**—It will be convenient to study here the methods which may be used for detecting and estimating damage in woollen materials. Damage of any kind is indicated by an alteration in the microscopic appearance of the fibre and in an increased solubility of its nitrogenous constituents in dilute alkalis or acids.

**Microscopic Detection of Damage.**—In an undamaged fibre every scale is perfectly distinct and its serrated edges plainly visible. Incipient damage by weathering, acids, alkalis, or bleaching agents is indicated by the outline of the scales becoming less distinctly marked and the serrated edges almost invisible. As the damage proceeds, the scales become marked with longitudinal ridges or striations, and ultimately disappear, exposing the cortex to view. The cortex may, in extreme cases, become frayed or ruptured, and stand out against the sides of the fibres. These stages of damage are seen in Figs. 102 and 103.

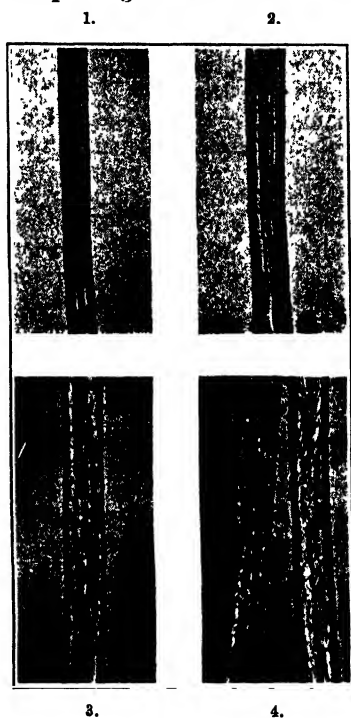


Fig. 103.—Damaged Fibres.

Damage is always accompanied by increased solubility of the wool-substance, and in many cases by the conversion of some of the loosely combined sulphur into sulphides.

The soluble wool-substance may be detected by means of the biuret reaction. If equal weights of damaged and undamaged wool are soaked in dilute (0.1N.) sodium carbonate solution, the quantity of nitrogenous matter which goes into solution is a measure of the damage. After about three hours, portions of the liquid are drawn off, acidified with dilute hydrochloric acid, and boiled to expel sulphuretted hydrogen. After cooling, a definite quantity of a dilute solution of copper sulphate is added, followed by excess of sodium hydroxide. When the precipitate has settled down, the supernatant liquid will have a violet colour if wool-substance is present, the depth of the colour being proportional to the quantity of dissolved nitrogen. The process may be made approximately quantitative by Becke's colorimetric method. For this purpose a standard solution of wool is made by dissolving 1 gram in sodium hydroxide, neutralizing with hydrochloric acid, boiling to expel sulphuretted hydrogen, and making up to a definite volume. To perform the test, volumes of this solution are measured into test-tubes, representing definite quantities of wool, *e.g.* ten quantities from 0.001 to 0.010 g. To these the same volumes of 0.05N. copper sulphate and 0.05N. sodium hydroxide solutions are added, and the precipitates allowed to settle. The solution to be tested is treated also with the same quantities of copper sulphate and sodium hydroxide, and the colour finally compared with those of the standards.

Still more accurate determinations may be made by estimating the dissolved nitrogen by the Kjeldahl process; or, alternatively, the soluble matter may be determined directly by drying a small portion of the sample and weighing it in a stoppered weighing-bottle. It is then soaked in the sodium carbonate solution, thoroughly washed, dried, and again weighed. The difference in the two weights gives the soluble matter.

Another useful method has been proposed by Becke (*J. Soc. Chem. Ind.*, 1912, 31, 386), particularly applicable to damage caused by alkalis. In such cases a part of the sulphur is converted into soluble sulphide, which is easily washed out, but another portion is retained in an insoluble condition in the fibre, which still gives reactions for sulphides. If undamaged wool is soaked in a solution of stannous chloride and acetic acid no reaction is obtained, but with alkali-damaged wool a brown stain of tin sulphide is produced, the depth of the brown colour being proportional to the amount of damage.

Allwörden's reaction is interesting, but in the hands of the authors has not proved reliable. He thinks that the valuable properties of wool fibre depend upon the presence of a substance which he terms *elastium*. This is said to be a carbohydrate found between the epidermis and cortex. Damaged fibres, according to Allwörden (*J. Soc. Chem. Ind.*, 1916, 35, 416), contain little or no *elastium*. He claims to have prepared *elastium* from wool by the following process: Five hundred grams of wool are wetted with hot water, and steeped for twenty-four hours in 8 litres of cold 0.2 per cent. sodium hydroxide. This dissolves the *elastium* together with some protein. The former is removed by dialysis, after which the solution of *elastium* is acidified with acetic acid, and concentrated on the water-bath to 200 ml. Sodium acetate and phenylhydrazine are now added, and the mixture is heated in boiling water. After an hour an osazone of *elastium* is thrown down as microscopic needle-shaped crystals with a melting-point of 188° C., apparently identical with the similar compound of galactose. The solution of *elastium* in acetic acid, after removal of the proteins, reduces Fehling's solution.

According to Allwörden the "elasticum reaction" enables incipient damage to be detected in its earliest stages, before structural damage of the fibres has been produced, since the first effect of any kind of damage is to cause the disappearance of the elasticum.

The test consists in mounting some of the fibres on a microscope slide in a half-saturated solution of chlorine-water, and examining them under a moderate magnification. The elasticum swells up, under the influence of the chlorine-water, forming a series of globular excrescences, which protrude through the epithelial scales along the whole length of the fibre (Fig. 104).

Incipient damage is indicated by the formation of relatively few swellings, while if none are formed the elasticum must have been completely destroyed. Kraus and Waentig (*J. Soc. Chem. Ind.*, 1920, **39**, 329A) observed that Allwörden's reaction does not give uniform results with all kinds of wool, and that different sections of the same wool react differently. Herbig (*J. Soc. Chem. Ind.*, 1919, **38**, 355A) found that the reaction is improved if bromine-water be used instead of chlorine. Grease must be removed first by extraction with benzene. Experiments made by the present authors showed the reaction to be somewhat uncertain. The positive effects are reliable, but wool known to be undamaged does not always give the globular swellings.

Damage in wool may be detected also by staining methods. Pauly used an alkaline solution of diazotized sulphanilic acid, which stains the cortex brown, but only when the epithelium has been damaged. A description of this method is given in the authors' *Textile Analysis* (Griffin & Co.), p. 168. Blackshaw (*J. Soc. Dyers Col.*, 1928, **44**, 298) recommended the use of Acid Scarlet 4R extra, which stains alkali-damaged fibres in a cold bath. Trotman, Bell, and Saunderson (*J. Soc. Chem. Ind.*, 1934, **53**, 267) found that staining with an acidified aqueous solution of Kiton Red G gave a quantitative method for the estimation of damage, and indigo carmine can be used in a similar manner. The Kiton Red process is as follows: 2 g. of the sample cut into small pieces is treated for 90 minutes at atmospheric temperature with 100 ml. of 0.005N. hydrochloric acid containing 0.5 millimol of Kiton Red G per 100 g. of wool. The liquor is then filtered through glass-wool, and the residual dyestuff in the filtrate determined by matching against a standard solution containing 0.1 millimol per litre. Undamaged wool absorbs about 0.143 millimol of dyestuff per 100 g. If preferred, the stained fibres may be counted under a microscope. In this case the numbers 1 and  $\frac{1}{2}$  are allotted to deeply and lightly stained fibres respectively. An example of a yarn and web damaged by chlorine is given in Table XXIV.

**Action of Heat on Wool.**—When heated to a temperature of 140° C., wool becomes discoloured, and it scorches at about 200° C. In the absence of air this is accompanied by the evolution of ammonia and sulphuretted hydrogen.

**Action of Light.**—The action of light on wool is due principally to the ultra-violet rays. This was investigated by Trotman and Taylor (*Analyst*, 1939, **64**, 406), who found that (i) a modification of the wool protein is produced which increases the solubility in alkalis and to a smaller extent in water; (ii) neutral wool is more susceptible to the action of light than either acid or

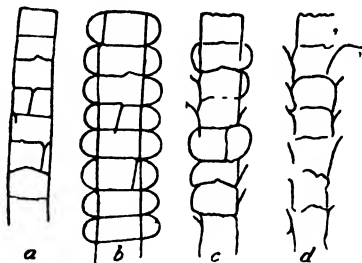


Fig. 104.—Wool Fibres treated with Chlorine Water.

a, untreated fibre; b, good fibre after treatment; c, damaged fibre after treatment, d, fibre from shoddy after treatment.



TABLE XXIV.—STAINING OF DAMAGED WOOL.

Specimen.	Dyestuff absorbed per 100 g., millimol.	Number of unstained Fibres.	Number of lightly stained Fibres.	Number of deeply stained Fibres.	Percentage damaged.
Untreated yarn	0.143	80	16	4	12
Chlorinated yarn	0.250	67	24	9	21
"    web	0.370	60	30	10	25
"    "	0.250	53	42	5	26
"    "	0.325	39	51	10	35.5
"    "	0.361	37	53	10	36.5
"    "	0.486	38	44	18	40
"    "	0.464	43	30	27	42
"    "	0.484	34	44	22	44
"    yarn	0.482	29	50	21	46
"    web	0.487	17	73	10	47.5
"    "	0.497	35	34	31	48
"    "	0.475	14	66	20	52
"    "	0.497	20	56	24	52
"    "	0.496	27	40	33	53
"    "	0.459	17	52	31	55
"    yarn	0.496	21	47	32	55.5
"    "	0.499	7	40	53	73

alkaline wool, and acid wool more susceptible than alkaline wool; (iii) the principal chemical change which takes place is the liberation of sulphuretted hydrogen, part of which is oxidized to sulphuric acid by contact with air or ozone formed at the surface of the wool. The rate of increase in acidity is seen in Table XXV.

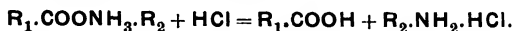
TABLE XXV.—EFFECT OF IRRADIATION ON ACIDITY OF WOOL.

Exposure to Ultra-violet Light, hours.	Acid, per cent.	Increase.
12	0.34	..
24	0.44	0.10
36	0.64	0.20
48	0.74	0.10
72	1.02	0.28

**Action of Acids.**—Cold concentrated sulphuric and hydrochloric acids dissolve wool slowly, more rapidly on heating, but in both cases decomposition takes place. Concentrated nitric acid acts very rapidly, nitrous fumes being evolved. Moderately dilute nitric acid produces yellow xanthoproteic acid. According to Raikow, cold syrupy phosphoric acid dissolves wool gradually with evolution of sulphur dioxide.

When wool is boiled with hydrochloric or sulphuric acid, it is hydrolysed

gradually to a mixture of amino acids, sulphuretted hydrogen being given off. Weak acids such as acetic acid have little destructive action. Speakman (*Proc. Roy. Soc.*, 1931, **A** 132, 167) has shown that acids have a peculiar action on the micelles of wool, in that the peptide chains within the micelle are separated, *i.e.* a kind of micelle subdivision takes place, this action being almost completely reversed by prolonged washing in running water. Further (Speakman, *J. Soc. Dyers Col.*, 1933, **49**, 189), salt linkages are broken and the chains separated by reactions of the type:



As mentioned above, wool combines chemically with acids. Firstly, the amino groups are neutralized, and secondly the CO.NH groups. With dilute solutions of mineral acids (*e.g.* hydrochloric acid) the total quantity of acid absorbed is only slightly in excess of that required by the amino nitrogen. With high concentrations of acid the CO.NH groups react also. According to Lloyd and Mayers (*Proc. Roy. Soc.*, 1932, **B** 69, 89), this occurs when the concentration of the acid exceeds 0.02N. The compound wool-acid is comparatively stable. It is almost impossible to free wool from acid by washing with distilled water; the assistance of a weak alkali is required. When wool is dyed with acid dyestuffs, sulphuric acid is used as an assistant. The concentration is insufficient to cause perceptible damage unless the wool has been damaged previously by alkali or other chemical. It may be noted here that incipient or actual damage caused in any process renders wool more likely to be damaged by another, and the cumulative effect may be considerable. Weak acids such as acetic acid and formic acid have little action on wool beyond opening up the structure of the micelles.

**Carbonization of Wool.**—The liability of acids to damage wool becomes of great importance in the carbonizing process. The object of this is to free the wool from burrs and other vegetable fragments, by converting them into hydrocellulose, which can be washed or shaken out. If burrs are not removed, they cause mechanical trouble in spinning and weaving. Moreover, they do not combine with acid dyestuffs, and thus cause light-coloured specks or patches in dyed goods, which have to be picked out or coloured by hand. But carbonization, since it consists in treatment with acid, affects the dyeing properties of the wool, and the acid is difficult to remove completely. Burrs constitute a great difficulty to be overcome. If they are not removed they cause trouble, as indicated above, while if removed by carbonization the wool may be damaged, made more susceptible to other kinds of damage, or may have a different affinity for dyes from that of ordinary wool, causing unlevel results.

Either an acid, such as sulphuric or hydrochloric acid, or a salt which produces acid by hydrolysis may be used. Sulphuric acid, hydrochloric acid, magnesium chloride, and aluminium chloride are the common agents. The latter two when dissolved in water give rise on drying to free hydrochloric acid; thus with magnesium chloride:



The goods are impregnated with a dilute solution of the reagent, and dried at a low temperature, depending on the chemical used and its concentration. The dried material is then baked at a temperature of from 150° to 212° F. (65.5°–100° C.) to change the cellulose into hydrocellulose, which is then removed by washing, the excess of acid being also washed out at the same time. The type of apparatus used is illustrated in Fig. 105.

The following is an example of the method used:

- (1) Impregnate with sulphuric acid of specific gravity 1.025.
- (2) Hydro-extract to remove the excess of acid.
- (3) Dry at 100° F. (37.8° C.), and then raise the temperature for two hours.
- (4) Wash.
- (5) Soak in dilute sodium carbonate solution.
- (6) Wash and dry.

If the wool is not well dried before raising the temperature to the carbonizing-point, there is danger of tendering. Harrison (*J. Soc. Chem. Ind.*, 1918, **37**, 264A) states that with sulphuric acid of an initial concentration of 5 per



Fig. 105.—Charlesworth Wool-drying or Carbonizing Machine.

cent. there is no danger, but that hydro-extracted wool must not be heated at 100° C. before it has been dried at a lower temperature, which should not exceed 77° C. With strengths up to 50 grams per litre there is no tendering after heating for two hours at 100° C., if the wool is dried first. With a concentration of 100 grams per litre tendering is pronounced during both drying and heating.

The addition of formaldehyde to the carbonizing solution is said to protect the wool from acid damage.

With burry and greasy wool, Hey (*J. Soc. Chem. Ind.*, 1920, **39**, 185A) recommends carbonizing *in the grease*, as the latter protects the wool from damage. The warm material from the drying-oven after carbonization is degreased, and the burrs are then crushed and shaken out. The acid is then removed by washing with water, followed by a solution of sodium carbonate, and finally with soap and water. The consumption of acid is greater than in the ordinary method of carbonizing after scouring, but the scouring predisposes the wool to acid damage. The following method of carrying out the process has been patented by Hey (*J. Soc. Chem. Ind.*, 1918, **37**, 409A).

Unscoured raw wool is steeped for one and a half hours in a bath containing 4·5 per cent. of sulphuric acid and 1 per cent. of 40 per cent. formaldehyde. It is then hydro-extracted, and dried at about 80° C. until the vegetable matter becomes friable. After drying, the carbonized wool is treated twice with a volatile organic solvent in a centrifugal degreasing machine, being centrifuged after each treatment. The adhering solvent is evaporated, the wool is then passed between fluted rollers, and the pulverized impurities are removed by opening and beating the wool in a current of air.

**Action of Alkalis on Wool.**—We have seen that wool has a fair amount of resistance to acids. With alkalis the case is quite different and alkaline damage is produced very easily. Strong alkalis, such as sodium and potassium hydroxide, attack it readily; milder alkalis, such as sodium carbonate, ammonium carbonate, and borax, have a less energetic action.

If wool is soaked in a cold (0° to 10° C.) concentrated solution of sodium hydroxide at 82° Tw. for about five minutes, and then washed immediately, it acquires an increased affinity for dyes without serious loss of tensile strength. Moreover, it does not shrink like cotton, and crimped effects in mixtures of wool and cotton may be produced by taking advantage of this fact. But if the wool is left in contact with the alkali it is quickly damaged. The epithelial scales are dissolved, exposing the softer cortex, which is in turn attacked, and the fibre gradually dissolves completely. The rate of solution depends upon the concentration and temperature of the alkali.

At ordinary temperatures the destructive effect is most rapid at a concentration of about 32° Tw. A boiling 2 per cent. solution of sodium hydroxide will dissolve wool in about five minutes. When wool dissolves in sodium hydroxide, it is completely hydrolysed into a mixture of amino compounds and sulphides. Owing to the presence of the latter the solution gives a black precipitate with a soluble lead salt. That is to say, wool does not dissolve in alkalis in the ordinary sense of the word, but is resolved by it into simpler soluble compounds.

The presence of formaldehyde, glue, or other colloid protects wool to a certain extent from damage by alkalis. Glue and similar bodies are used under the name of *protective colloids* in dyeing for this reason.

*Mild alkalis* have a less deleterious effect on wool than sodium hydroxide, but temperature and concentration are important factors in determining the extent of damage produced. Sodium carbonate is used in wool-scouring, either with or without soap. Scoured wool sometimes contains more than occasional damaged fibres. Damage produced in subsequent processes is often due to incipient damage caused by sodium carbonate in scouring. Ammonia, ammonium carbonate, and borax are the safest alkalis to use. Wool has sometimes to be dyed in a faintly alkaline bath; in such cases borax should, if possible, be made use of.

**Action of Wool on Solutions of Soap.**—Wool has the power of adsorbing soap from its aqueous solutions. The difficulty of removing all traces of soap from wool after scouring is well known. According to Woodmansey (*J. Soc. Dyers Col.*, 1919, 35, 169), there is a preferential adsorption of the acid constituents, and this increases with the concentration and time of action of the soap solution. The following amounts of fatty acids were taken up from a 1 per cent. solution of Castile soap:

Crossbred serge	3·6 per cent.
Spun-silk yarn	1·8 "
Cotton-wool	1·4 "
Cotton cambric	0·4 "

More recent work by the Wool Research Association (*J. Soc. Chem. Ind.*, 1922, 41, 626A) is of interest. Wool was purified by scouring with potash, olive-oil soap, and sodium carbonate, and then extracting three times with absolute alcohol. The wool thus purified was immersed in a soap solution for a definite time and at a fixed temperature. The loss of alkali and fatty acids in the soap solution was then determined. It was found that more of the basic portion of the soap was adsorbed than of the fatty acids, so that an acid soap, e.g.  $C_{17}H_{35}COONa.C_{17}H_{35}COOH$ , remained in the bath. But this is accompanied by the adsorption of the soap as a whole. The fatty acids liberated by preferential adsorption of alkali are partly precipitated on the wool. The precipitation of fatty acids decreases with increase in concentration, owing to the soap acting as a protective colloid. Thus in concentrated soap solutions the chief action is adsorption of soap only. The action continues for several days, and is accelerated by increase of temperature. During the early stages, the rate of loss of alkali by the soap solution is greater than that of fatty acids, but the difference lessens with time, and gradually disappears. In the case of mixtures of soaps of oleic and palmitic acids there is a preferential adsorption of the oleic-acid soap, but there is no difference between the rates for sodium and potassium soaps. The adsorption of alkali by wool from a chemically neutral soap is equal to that from a solution of sodium hydroxide of much lower concentration. The ratio of concentration of sodium hydroxide solution to that of a soap solution giving the same adsorption increases with increasing dilution. In treating wool with alkaline soap liquors, the advantage of free sodium carbonate may be due to its action in increasing emulsification, and also in opposing the liberation of fatty acids.

Commercially scoured woollen goods frequently contain much unremoved soap, amounting to 2 per cent. and over. Much of this can, however, be washed out with hot water if the washing is conducted in the proper manner. In washing fabrics it should always be remembered that two washings with small quantities of hot water are more effective than one with a large volume.

The amount of soap retained by a fabric seems to depend upon the nature of the fatty acids present in the soap used. With fatty acids of low titer the quantity is very small; with sulphonated oils it is practically nil.

**Estimation of Residual Soaps.**—This is carried out by the Wool Research Association in the following way: The sample is extracted twelve times in a Soxhlet with alcohol. The solution is then filtered, the alcohol evaporated, and the residue dried and weighed. After weighing, the soaps are boiled with a measured excess of decinormal sulphuric acid, cooled, and transferred to a separating-funnel. The fatty acids are extracted with ether and weighed. The residue is then dissolved in alcohol, and the fatty acids are checked by titration. The soap is determined in the aqueous extract by titrating with decinormal alkali and calculating the difference to sodium oleate.

**Action of Wool on Solutions of Salts.**—When wool is boiled with a solution of alum, or of many other salts of the heavy metals having an acid reaction, the salt is hydrolysed into a basic and an acid portion, the wool fibre combining with the former and retaining it permanently. This is the basis of the process of *mordanting*. The acid portion of the salt is thought by some observers to be adsorbed, simultaneously combining with the basic groups of the wool. Others hold that the acid portion remains entirely in the solution. Paddon (*J. Soc. Chem. Ind.*, 1922, 41, 978A) states, however, that no definite chemical compound is formed when wool is mordanted with alum, but that the action is one of adsorption in which both alumina and sulphuric acid are involved. Similar results have been obtained by Bancroft in the case of chromium mordants.

**Action of Dyes on Wool.**—Wool has a marked affinity for dyes. It is dyed directly by the acid, basic, and direct dyes. Its affinity is, however, not marked at temperatures below 140° F. (60° C.), and is fully developed only at the boiling-point.

**Action of Bleaching Agents on Wool.**—Reducing bleaching agents, such as sulphur dioxide or sulphurous acid, seem to form leuco compounds with the natural colouring-matters of wool, regenerating the colour gradually upon exposure to air. At the same time sulphur dioxide is adsorbed and retained by the fibre. Wool is often bleached with sulphur dioxide. The processes will be described later.

Among oxidizing bleaching agents hydrogen peroxide and sodium peroxide also are used. In limited quantities they have no deleterious effect upon the wool, but in excess they gradually act in the same way as ozone, destroying the epithelial scales. Potassium permanganate acts in the same way.

Chlorine or hypochlorites cannot be used for bleaching wool, since they rapidly attack the wool-substance, forming both soluble and insoluble chloramines. This is accompanied by destruction of the epithelial scales and solution of sulphur as sulphuric acid. If wool is treated with excess of chlorine-water, it takes up about 30 per cent. of chlorine, but is entirely changed into a yellow pulpy mass. Chlorine and hypochlorites are, however, employed in the *chlorination* process for rendering woollen garments unshrinkable.

**Action of Formaldehyde.**—When wool is treated with an aqueous solution of formaldehyde, combination takes place, the maximum quantity taken up being 0.7 per cent., at a temperature of about 70° C. Trotman, Trotman and Brown (*J. Soc. Dyers Col.*, 1928, 44, 47) found that treatment with formaldehyde increased the resistance of wool to attack by alkalis and acids. A sample of the treated wool was soaked in 0.05N. sodium hydroxide solution for 12 hours. The filtered liquid gave no biuret reaction, and nitrogen could not be detected by the Kjeldahl method. Similarly, boiling with 0.5 per cent. sulphuric acid caused no loss of nitrogen. The affinity for neutral-dyeing acid dyestuffs was reduced greatly. In the presence of sulphuric acid dyeing was accompanied by evolution of formaldehyde, but the shrinkage during dyeing was reduced considerably.

**Action of Micro-organisms.**—Wool is attacked readily by micro-organisms under suitable conditions, *i.e.* in the presence of alkali, moisture, and warmth. It is particularly susceptible to the growth of moulds, which generally cause discolorations and a musty odour. The degree of alkalinity favouring growth is about pH 8. The growth of moulds or bacteria is of course accompanied by the production of proteolytic enzymes, which decompose the keratin, forming soluble nitrogenous compounds. Trotman and Sutton (*J. Soc. Dyers Col.*, 1925, 41, 27) found that, among bacteria, spore-forming bacilli and those which liquefy gelatin cause most damage. Different organisms produce damage at different rates, each being most active between definite limits of pH. Damage is accompanied by destruction of the epithelial scales and ultimately by disintegration of the fibre. Goods damaged by micro-organisms have an increased affinity for acid and basic dyestuffs, but dye unevenly. They have also an increased solubility in water, dilute alkalis, and acids. Storage in a damp, warm atmosphere is the common cause of this kind of damage.

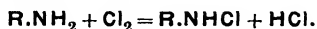
**Action of Chlorine and the Chlorination of Wool.**—Dry wool absorbs both gaseous chlorine and chlorine from a solution in carbon tetrachloride. According to Meunier and Latreille (*Chim. et Ind.*, 1923, 10, 636), 4.4 per cent. of chlorine is taken up, sulphur chloride and chloramines of the type

$R.NHCl$  being formed (*see below*). When moisture is present, or a solution containing chlorine is used, oxidation of the protein takes place also. If the absorbed chlorine be removed by means of a dechlorinating agent, the wool will be found to have a greatly diminished power of shrinking and felting. This action of chlorine on wool is important, because it is made use of to produce what is known as the *unshrinkable finish*. The chief disadvantage of wool as a textile fibre is that fabrics made with it shrink and felt when treated with hot water or soap and water. This is made use of to a certain extent in the milling of knitted goods and cloth, but subsequent felting or shrinking is a serious objection. The cause is not fully understood, but it is undoubtedly connected with the interlocking of the free edges of the epithelial scales, since anything which rounds these off diminishes felting power.

Wool felts and shrinks more readily in acid or alkaline solutions than in water or a neutral solution. It has been suggested by Speakman and Astbury that felting is accounted for by the combination of the peculiar molecular structure of the wool protein and the properties of the epithelial scales. The structure of the keratin molecule in the absence of acids or alkalis resembles a spiral spring in which the individual segments of the spiral are bound together by links which prevent expansion or contraction. These links are, in fact, the side-chains which have been already described. In the presence of acids and alkalis these are severed, and the molecule, and with it the fibre, is free to expand or contract along its longitudinal axis. Felting is always brought about by mechanical forces which cause alternate compression and relaxation of the wool fibres—that is, the fibre is continually subjected to elongation and contraction. The scales, the projecting free edges of which point towards the tip of the fibre, allow the latter to slide over each other when they expand, but they become interlocked when the fibres contract, thereby continually drawing them closer together. This causes the thickening and contraction associated with felting.

Chlorine and other oxidizing agents such as ozone, which attack the free edges of the epithelial scales, also diminish felting power and shrinkage. Enzymes act in a similar manner. The action of chlorine was observed first by Knecht, who patented a process for producing crimped effects based upon this property. Fabrics were printed with a thickened solution of sulphuric acid, and then passed through a solution of bleaching powder. When soaped, the printed parts remained unchanged, whilst the untreated portions shrank, thus producing a permanent crimped effect. The use of chlorine for the production of an unshrinkable finish developed from this observation.

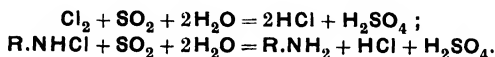
When wool is treated with an aqueous solution of chlorine, the chlorine is absorbed, and if excess of chlorine be present, the wool is transformed gradually into a yellow pulpy mass. Part of the chlorine is merely adsorbed, the remainder combining with the wool protein to form a chloramine by reacting with the primary amino group. Thus:



At first, only insoluble chloramines are produced, but if the action is prolonged or excess of chlorine is present, soluble nitrogen compounds are formed. These are accompanied by the production of a yellow colour and a soft or slimy handle. At the same time sulphuric acid is produced by oxidation of the sulphur of the cystine residue.

If the quantity of chlorine is limited and a dilute solution used, the action can be controlled, and a considerable degree of unshrinkability produced without serious damage to the fabric. The quantity of chlorine necessary to

produce a reasonable degree of unshrinkability varies from 3 to 5 per cent. on the weight of the goods according to the quality of the wool. Either bleaching powder or sodium hypochlorite may be used, together with sufficient hydrochloric acid to liberate the available chlorine. The scoured goods are worked in this cold solution for about 20 minutes. They are then washed in water, and passed into a cold dechlorinating bath. This may contain sodium sulphite, sodium bisulphite, or sulphurous acid, but the best is a mixture of sodium bisulphite and bicarbonate. The following reactions now take place:



When dechlorination is complete, the goods are washed with water, treated with soap and a little ammonia or sodium bicarbonate to neutralize acid, and again washed with water. Great care must be taken to remove the goods from the chlorinating bath before a yellow colour or slimy handle appears. This danger can be avoided by limiting the concentration of the chlorine to 0.5 to 0.6 g. per litre.

In practice, difficulty is often experienced in obtaining uniform unshrinkability throughout a batch. This is due to the rapidity of the reaction. One hundred pounds of wool in a machine will absorb 3 lb. of chlorine in about 80 seconds, so that, naturally, those parts of the fabrics which offer most resistance to penetration will be undertreated, whilst other parts will be over-treated. In order to obtain uniform results, the following conditions must be ensured: (i) the goods must be thoroughly wetted before the hypochlorite is added; (ii) the machine used must allow free movement of the goods, and there must be a high degree of agitation; (iii) chemicals must be well diluted before being added to the bath; and (iv) they must be added slowly.

It is important that an excess of acid should be present. If the liquor becomes neutral or alkaline, discoloration of the fabric occurs. It is impossible to say how much chlorine any fabric will require to render it unshrinkable. For any material with which the process has not been established by previous experience, small-scale preliminary experiments should be made. Botany wools require more chlorine than crossbred wools. There are, however, factors other than the percentage of chlorine to be considered. The tightness of the packing of the fibres within the yarn plays an important part. When it is loose, there is more freedom for the fibres to expand and contract. This gives greater scope for the mechanism described above to come into operation. Thus, a twofold yarn shrinks more than a single-fold yarn. Loose twist in spinning and slack weaving or knitting make more chlorine necessary to give unshrinkability than is the case with tight twist or stiff fabric structure.

**Structural Changes in Wool Fibre accompanying the Chemical Action of Chlorine.**—To begin with, the free edges of the fibres become less evident, and ultimately disappear. After this point has been reached, the scales become thin and semi-transparent, and longitudinal markings are seen, which are caused by the exposure of the spindle-shaped cortical cells. This is the point at which the yellow, slimy condition is noticed. If the action of the chlorine is continued, the scales disappear, and the cortex is completely exposed, and may become completely disintegrated. These effects are illustrated in Figs. 106 and 107.

The difficulty of the process is that these changes may take place simultaneously, particularly when two or more kinds of wool are present. Moreover, if the process is not carried far enough the goods will not be sufficiently unshrinkable, while, on the other hand, if chlorination is pushed far enough to



give complete unshrinkability, there is always a danger of producing a considerable percentage of badly damaged fibres, accompanied by loss of weight

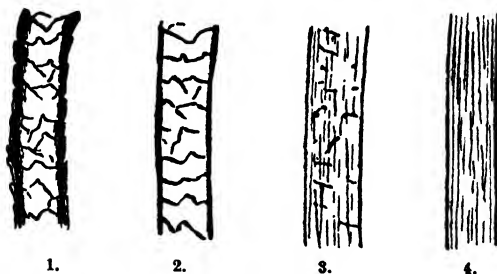


Fig. 106.—Action of Chlorine on Wool Fibres.

1. Untreated wool fibre.
2. First stage of chlorination.
3. Second stage, showing incipient damage.
4. Third stage, showing complete destruction of epithelial scales.

and wearing power. It may be noted that the presence of metallic catalysts such as copper and iron accelerates the destruction of the fibre.

Since chlorination produces both structural damage and chemical modification of the wool protein, fabrics treated by this process are apt to have diminished wearing power, and this is especially noticeable when there is much structural damage. This means that, although the goods may not



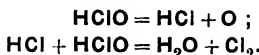
Fig. 107.—Spindle Cells from Disintegrated Wool Fibre.

shrink or felt, they wear badly. Speakman and Goodings (*J. Text. Inst.*, 1926, **17**, T 606) state that the reduction in shrinkage and wearing power is due to the formation of a layer of jelly between the cortex and epithelium by the consecutive actions of chlorine and soda. The bad wearing properties associated with the treated wool are due to the ease with which this layer and its surrounding scales are removed by friction. This can be prevented by mordanting the treated wool with potassium dichromate.

There is another difficulty to be overcome, namely, that of even treatment of the fabric. This, however, arises chiefly from using concentrated solu-

tions of chlorine for a short time, instead of dilute solutions for a longer period.

It was shown by the authors (*J. Soc. Chem. Ind.*, 1931, **50**, 463r) that (i) the damage produced depends largely upon the pH of the chlorinating bath; and (ii) hypochlorous acid produces the same effect as chlorine, but very little damage. A solution of hypochlorous acid having an acidity not greater than that represented by pH 6 gives unshrinkability accompanied by less than 10 per cent. of damaged fibres. But solutions of hypochlorous acid gradually give hydrochloric acid, and then chlorine, in accordance with the equations:



It was found that the addition of a little phenol to the bath inhibited these changes, and reduced damage to 5 per cent. without affecting the unshrinkability. The chlorinating bath is prepared by treating bleaching powder solution with excess of boric acid and adding 0.5 per cent. of phenol on the weight of the goods. Similar results (Trotman, *J. Soc. Chem. Ind.*, 1933, **52**, 150r) were obtained with chlorine-water and sodium acetate, and by chlorinating at 100° F. (37.8° C.) less chlorine is required than at atmospheric temperatures. This is seen in Table XXVI. It must be remembered, however, that if the pH of the bath is less than 6, discoloration may be produced.

TABLE XXVI.—EFFECT OF TEMPERATURE ON CHLORINATION OF WOOL.

Concentration of Chlorine-water, per cent.	Temperature, ° F.	Percentage of Damaged Fibres.
2	60	10
1	100	10
1	140	10

Further experiments (Trotman and Bell, *J. Soc. Chem. Ind.*, 1935, **54**, 30r) indicated that the substitution of bromine for chlorine has distinct advantages. It gives a high degree of unshrinkability, a good handle, and very little damage. The solution is buffered with sodium acetate. It should be noted, however, that Callan (*ibid.*, 1935, **54**, 544r) had also used bromine, but without sodium acetate. The results obtained in large-scale experiments are given in Table XXVII. Neither tensile strength nor extensibility showed any decrease in the samples of yarn treated with bromine; in fact, a slight increase in both was found.

TABLE XXVII.—BROMINATION OF WOOL.

Reagent employed.	Percentage of Bromine absorbed.	Percentage of Damaged Fibres.
3 per cent. Br <sub>2</sub> . . .	100	2.6
3 per cent. Br <sub>2</sub> . . .	100	2.9
5 per cent. Br <sub>2</sub> + NaAc . .	100	5.0
10 per cent. Br <sub>2</sub> + NaAc . .	100	7.0

The Wool Industries Research Association has patented a plant in which gaseous chlorine is used. The goods are packed in an airtight autoclave, from which the air is evacuated. A measured quantity of chlorine gas is then introduced through a perforated tube placed in the centre of the chamber. The advantages claimed for this process are (i) since the chlorine enters a vacuum containing the wool, there is complete and uniform penetration, whilst in wet processes there is danger of only surface action taking place; and (ii) the wet process is not suitable for treating tops before spinning, because the movement of the goods makes spinning difficult without excessive waste. It is an advantage to be able to spin yarn from unshrinkable wool. The mixing of the treated wool during spinning would prevent lack of uniformity from being apparent.

The results obtained by this process are affected to a considerable extent by the moisture content of the wool when it enters the autoclave. Precautions should be taken to bring the material to a definite predetermined condition before treatment.

Another important and recently patented process is that of Adams and Hall. The dry material is treated for an hour in a solution of sulphuryl chloride in white spirit. This is made up to about 2 per cent. concentration, but the actual strength depends upon the type of material and degree of unshrinkability desired. The wool must be dried carefully before treatment, drops of water left in the goods causing holes to appear. In practice, the goods are allowed to stand in a room in which the relative humidity of the atmosphere is kept constant by means of a conditioning unit until equilibrium is reached. This is necessary, because variation in water content affects the results. After treatment with the sulphuryl chloride the goods are hydro-extracted, and the spirit is collected and returned to the storage tank. After this, the goods are transferred to a vessel containing water and alkali, and then washed with water.

For further information on recently evolved methods of producing unshrinkable finishes, see p. 526.

**Properties of Chlorinated Wool.**—These depend, naturally, upon the degree of chlorination. Moderately chlorinated samples have an increased affinity for water, i.e. a greater regain, and are wetted more readily than untreated wool. The increased affinity for water is seen from Table XXVIII, which shows the percentage absorbed when dry samples were exposed to air.

TABLE XXVIII.—REGAIN OF CHLORINATED WOOL.

Time, days.	Good Sample, regain, per cent.	Bad Sample, regain, per cent.
1	9.76	12.40
3	16.16	18.04
6	16.80	19.07

Over-chlorination produces an increased solubility in alkalis, acids, and perspiration. When a good sample is soaked in 0.1N. sodium hydroxide solution it swells but retains its firmness. Bad samples, on the other hand, assume a "fallen" appearance, and gradually break down, a considerable amount of protein being dissolved (Table XXIX). This solubility and "falling" of damaged goods forms one of the chief causes of bad wearing. Every time the goods are washed they are soaked in dilute solutions of alkali. Gradually

more and more of the wool-substance is dissolved, until ultimately the fibre breaks down. The solubility in artificial perspiration is of considerable importance as a factor affecting wearing properties. It is much less marked than the solubility in alkaline solutions, but is still quite distinct. It is always greater in the case of damaged goods. Untreated and well treated wool lose only traces of nitrogen even when soaked in dilute acetic acid and salt solutions for long periods. Damaged chlorinated wool, on the contrary, gives a biuret reaction in a comparatively short time.

TABLE XXIX.—SOLUBILITY OF BADLY CHLORINATED WOOL.

Damage, per cent.	Amount dissolved in	
	0.1N. Sodium Hydroxide, per cent.	Acetic Acid + Salt, per cent.
5	3.51	0.9
25	9.60	4.00
50	14.50	6.20

Chlorinated wool is said to have an increased affinity for acid dyestuffs, but it was shown by Trotman and Bell (*J. Soc. Chem. Ind.*, 1935, **54**, 29r) that this is only apparent. If dyeing is begun in a cold bath and carried out in the same manner as for silk, there is no difference between the affinity of treated and untreated samples.

**Chemical Tests.**—The following are the most important chemical tests for chlorinated wool:

*Solubility in Decinormal Sodium Carbonate.*—About 2 g. of the sample is soaked for 6 hours in 100 ml. of decinormal sodium carbonate. At the end of this period 5 ml. of the liquor is placed in a test-tube, and acidified with hydrochloric acid. A fixed volume of a standard copper sulphate solution is then added, followed by excess of sodium hydroxide. After the precipitate has settled, the colour of the solution is noted or compared with that obtained from a known quantity of wool solution. The soluble matter may be determined directly by the following method:

The sample is dried, weighed in a weighing-bottle, and soaked as above in sodium carbonate solution. It is then washed with hot distilled water till free from alkali, dried, and again weighed. The loss in weight gives the soluble matter.

*Saur's Wearing Test.*—0.5 g. of the wool is treated with 40 ml. of water, 50 ml. of 1-volume hydrogen peroxide, and 10 ml. of 0.5N. potassium hydroxide solution for 3 days. The liquid is then filtered, and the dissolved nitrogen determined in an aliquot portion of the filtrate.

**Estimation of Damaged Fibres.**—Damage is determined generally by microscopic examination. A few fibres are teased out, mounted in water on a microscope slide, and examined, partly damaged fibres being counted as  $\frac{1}{2}$  and badly damaged as 1. At least 100 fibres taken from different parts of the material should be examined. The sum of the damaged and partly damaged fibres is returned as a percentage.

*A modified Pauly test* was recommended by Rimington (*J. Text. Inst.*, 1930, **21**, r 237), and this stains damaged fibres brown, the depth of colour depending on the degree of damage. The reagents required are—

Sodium sulphanilate	. . . . .	10 per cent.
Sodium hydroxide	. . . . .	10 "
Sodium carbonate	. . . . .	9 "
Sodium nitrite	. . . . .	8 "
Concentrated hydrochloric acid		
Naphthalene Leather Brown BS (I.C.I.).		

A weighed quantity of the wool is wetted with 15 ml. of the sodium carbonate solution in a test-tube, while 10 ml. of the sodium sulphanilate solution and 5 ml. of the sodium nitrite solution are mixed in a second test-tube; 2 ml. of concentrated hydrochloric acid is added to the first test-tube, which is allowed to stand for 1 minute, after which the sulphanilate-nitrite mixture is added. After standing for 1 minute the wool is removed and rinsed in water. It is then treated with 4 ml. of the sodium hydroxide solution, and heated for 5 minutes in boiling water. The solution is then made up to a definite volume with water, and the colour matched with a standard solution of the dyestuff. This method was examined critically by Edwards (*J. Text. Inst.*, 1933, **24**, r 1), who found that it was not sufficiently reliable to replace the microscopic test.

The *Kiton Red G* method of Trotman, Bell and Saunderson (*J. Soc. Chem. Ind.*, 1934, **53**, 265r) described above, p. 175, may be used also. The Wool

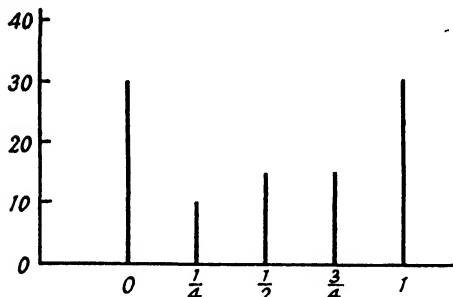


Fig. 108.

Industries Research Association recommend the following procedure: A 1-g. representative sample of fibres taken from the fabric is shaken in a mechanical shaker for 60 minutes with 100 ml. of a solution prepared by dissolving 0.615 g. of anhydrous *Kiton Red G* containing 94.8 per cent. of pure dyestuff and 100 ml. 0.1N. hydrochloric acid in 2 litres of distilled water. At the end of this period the wool is removed, rinsed free from loose dyestuff, and dried. The

dyed sample is then wound spirally round a wooden pencil, and a longitudinal cut is made along it by means of a cutter consisting of two "Valet" safety-razor blades clamped together in such a manner that a cut made with it removes a large number of fibre samples of uniform length (approximately 0.3 mm.). The fibre cuttings between the blades are scraped out into a drop of B.P. paraffin on a microscope slide, well mixed, and covered with a cover-glass. They are then examined microscopically, using an 8-mm. objective and a  $\times 6$  eyepiece. By means of a travelling stage the slide is traversed systematically until 100

Degree of Damage.	Percentage of Fibres.
0	30
1/4	10
1/2	15
3/4	15
1	30

fibre sections have been examined, each being assigned to one of five classes according to whether they are stained white, light pink, pink, pink-red, or deep red. These classes are designated respectively 0,  $\frac{1}{4}$ ,  $\frac{1}{2}$ ,  $\frac{3}{4}$ , and 1. The results obtained may be represented diagrammatically as in Fig. 108.

**Testing of Shrinkage.**—It is important for the purpose of works control to have a standard method of testing the shrinkage of treated materials. Various processes are used, such as treatment in a mill or domestic washing-machine with soap and water for a definite time. In order to obtain reliable results great care must be taken to standardize the conditions of the test. A suitable method (*J. Text. Inst.*, 1939, **30**, 22) is as follows: The test consists of the measurement of (i) the relaxation and (ii) the felting power.

**Relaxation.**—Fabrics are often subjected to strains and tension during manufacture or finishing. These are temporary, and are released when the material is wetted, thus producing a relaxation or contraction during the first washing or immersion in water. Shrinkage caused in this manner must be distinguished from that due to felting, and the "unshrinkable-finish" processes prevent shrinkage of only the latter type. Hence, in a standard test, relaxation should be measured first, and shrinkage due to felting should be expressed as a percentage of the relaxed area.

Relaxation shrinkage is measured in the following manner: A square piece of the material is taken, and a reference square marked upon it with red cotton or marking ink. This square is measured, and the piece is soaked for  $1\frac{1}{2}$  hours in a freshly prepared solution containing 0.3 per cent. of sodium oleate and 0.5 per cent. of sodium sesquicarbonate at a temperature of  $35^{\circ}$  to  $37^{\circ}$  C. The water used throughout the experiments should be of zero hardness. After this soaking, the sample is rinsed with water, and then measured under water. This is done by placing it in a flat dish containing about half an inch of water and measuring the length and breadth of the marked area with a stainless-steel ruler. The above process is repeated, the time of soaking being reduced to half an hour, until no further relaxation occurs.

**Shrinkage due to Milling.**—The relaxed sample is passed through a wringer, and soaked in a freshly prepared 10 per cent. solution of sodium oleate at  $35^{\circ}$  to  $37^{\circ}$  C., after which it is again passed through the wringer until the weight of the solution retained is from 50 to 70 per cent. of the weight of the air-dry specimen. The sample is then placed in the cylinder described below with the requisite number of balls, and the machine is rotated for  $2\frac{1}{2}$  hours. The sample is then rinsed, and measured under water as in the relaxation test.

The milling apparatus consists of a stainless-steel cylinder having an internal length of 26 cm. and a volume of 2 litres. The cylinder is mounted on a horizontal axle so that it can rotate in a bath, which is kept at a temperature of  $35^{\circ}$  to  $37^{\circ}$  C., making five revolutions in alternate directions at a rate of 32 to 34 revolutions per minute. Steel balls of  $\frac{3}{4}$ -inch diameter coated with  $\frac{1}{8}$  inch of vulcanized rubber are placed in the cylinder with the sample, the number of balls being

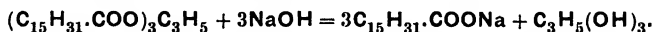
For specimens weighing 35 g.	.	.	.	.	7 balls
" " 30 g.	.	.	.	.	6 "
" " 25 g.	.	.	.	.	5 "
" " 20 g.	.	.	.	.	4 "
" " 15 g.	.	.	.	.	3 "

## CHAPTER XV.

### OILS, FATS, AND WAXES—SOAPS—WETTING AGENTS— WATERPROOFING AGENTS.

#### Oils, Fats, and Waxes.

OILS and fats are triglycerides of various fatty acids, which include solid fatty acids such as palmitic acid,  $C_{15}H_{31}.COOH$ , and stearic acid,  $C_{17}H_{35}.COOH$ , and liquid fatty acids like oleic acid,  $C_{17}H_{33}.COOH$ . The triglycerides of these are *tripalmitin*,  $(C_{15}H_{31}.COO)_3C_3H_5$ , *tristearin*,  $(C_{17}H_{35}.COO)_3C_3H_5$ , and *triolein*,  $(C_{17}H_{33}.COO)_3C_3H_5$ . Tripalmitin and tristearin are solid at ordinary temperatures, whilst triolein is liquid. These three triglycerides are present in all fats and oils, and the proportions of solid and liquid triglycerides determine whether the substance is a fat or an oil; *i.e.* a fat consists largely of solid triglycerides, while in an oil the liquid triglycerides preponderate. Small quantities of other triglycerides are present also, and these give the oil or fat its special properties. For example, butter fat contains tributyrin,  $(C_3H_7.COO)_3C_3H_5$ , and castor oil a triglyceride of ricinoleic acid,  $C_{17}H_{32}(OH).COOH$ . When an oil or fat is heated with a solution of a caustic alkali, it undergoes a process termed *saponification*, giving the sodium salt of the fatty acid, which is a *soap*, and glycerol, thus:

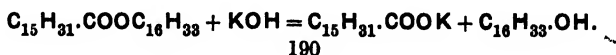


A *wax* is a compound of a fatty acid with a solid monohydric alcohol. Examples of such alcohols are given in Table XXX. A wax is difficult to

TABLE XXX.—ALCOHOLS OCCURRING IN WAXES.

Name.	Formula.	Melting-point, ° C.	Occurrence.
Cetyl alcohol .	$C_{16}H_{33}.OH$	50	Spermaceti.
Ceryl „ .	$C_{26}H_{53}.OH$	79	Chinese wax.
Melissyl „ .	$C_{30}H_{61}.OH$	88	Beeswax.
Carnaübyl alcohol .	$C_{24}H_{48}(OH)_2$	103	Carnaüba wax.
Gossypyl „ .	$C_{30}H_{61}.OH$	87 to 88	Cotton.

saponify, but when heated under pressure with alcoholic caustic potash, it is decomposed slowly, giving soap and the solid alcohol. Thus cetyl palmitate reacts as follows:



*Paraffin wax* is not a true wax. It cannot be saponified. It contains neither fatty acids nor alcohols, but consists entirely of hydrocarbons which are unaffected by boiling with caustic alkalis, and are termed *unsaponifiable*.

Thus we have three classes, viz. (i) fats and oils, readily saponified, giving glycerol as one product; (ii) waxes, difficult to saponify, yielding solid alcohols; and (iii) unsaponifiable oils and waxes. Members of each of these classes are of importance in the textile industries.

**Properties of Oils, Fats, and Waxes.**—All of these are insoluble in water, and when mixed with it merely float upon its surface. They are, however, readily soluble in organic solvents such as chloroform, ether, petrol, benzene, and chlorinated hydrocarbons. They also form emulsions when agitated with water containing soap or other emulsifying agents.

Oils and fats can be removed from textile materials in three ways:

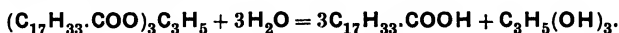
- (1) By saponification when the fabric is not damaged by alkalis, as in the case of cotton.
- (2) By emulsification with soap and water when the fabric (*e.g.* wool) would be attacked by alkali.
- (3) By extraction with an organic solvent, as is done in *dry cleaning*.

Sometimes, two methods are used simultaneously. For example, a hot solution of soap and water containing a hydrocarbon such as toluene or xylene effects both emulsification and dissolution.

**The Fatty Acids.**—The physical nature of an oil or a fat is determined by the proportions of solid and liquid triglycerides, while the chemical properties depend upon the individual acids present. Fatty acids may be either saturated or unsaturated compounds. Palmitic and stearic acids are derivatives of the paraffin series of hydrocarbons and are saturated. Stearic acid is represented by the formula  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ . Oleic acid is an unsaturated compound derived from a member of the olefine series of hydrocarbons, and has the formula  $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$ . When an unsaturated fatty acid is treated with hydrogen in the presence of a catalyst, it becomes saturated. Thus oleic acid is changed into stearic acid,  $\text{CH}_3(\text{CH}_2)_8(\text{CH}_2)_8\text{COOH}$ . Solid fats are made from liquid oils in this way. Unsaturated fatty acids are also readily oxidized to compounds known as *hydroxy fatty acids*. When oleic acid is oxidized in the presence of moisture it is changed into dihydroxystearic acid, which is a saturated compound:



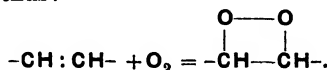
All oils and fats are hydrolysed by lipolytic enzymes with the production of free fatty acids and glycerol:



Liquid oils, such as olive oil, which contain a large amount of liquid fatty acids are liable to become *rancid*, a frequent cause of trouble in the scouring and dyeing of textile goods. The development of rancidity is favoured by (i) the presence of free fatty acids, (ii) access of air, (iii) the presence of moisture, (iv) traces of catalysts such as iron or copper, (v) organic matter which may contain lipolytic enzymes, and (vi) an elevated temperature. The first stage in the production of rancidity is the formation of free fatty acid by the action of enzymes in the presence of moisture. This free fatty acid then absorbs oxygen, forming a hydroxy fatty acid in the manner described above. The further action of oxygen assisted by oxidizing enzymes gives rise to aldehydes or ketones derived from the glycerol which has been liberated by hydrolysis.



Among these are acrolein,  $\text{CH}_2\text{:CH.CHO}$ , and cœnanthal aldehyde,  $\text{C}_6\text{H}_{13}\text{.CHO}$ . Lastly, oxidation at the double bond produces bodies having the nature and properties of peroxides, thus :



Rancid oil may be the cause of much trouble in the scouring or the dyeing of textile goods. Oxidized fatty acids and their peroxides are highly coloured compounds, and are very difficult to remove by any ordinary scouring process, especially in the case of woollen goods. If not removed they inhibit bleaching and cause also uneven dyeing. Yarn on its way to a knitting machine is lubricated, generally, by passing it through an emulsion of olive or neatsfoot oil. After knitting, the goods may be kept in a warm atmosphere for some time before being scoured or dyed. During this interval the oil is liable to become rancid, with the results described above, even if the oil itself was not rancid before. A small quantity of an *anti-oxidant*, such as  $\beta$ -naphthol, is sometimes added to an oil to delay the development of rancidity.

**Detection of Rancidity.**—*Aldehydes* can be detected by the Kreis reaction : 10 ml. of the oil is shaken with 10 ml. of hydrochloric acid and a few drops of a 1 per cent. alcoholic solution of phloroglucinol until completely emulsified. The mixture is then allowed to stand. If aldehydes are present, the lower layer will be coloured pink.

*Ketones* are detected as follows: The oil is distilled with steam into salicylaldehyde (purified by treatment with sodium bisulphite). The distillate is shaken, and to the emulsion which separates a little concentrated sulphuric acid is added. When ketones are present a red colour will be produced.

*Peroxides* liberate iodine from an acid solution of potassium iodide. The Taffel and Revis test may be used : 10 g. of the oil, 40 ml. of acetic acid, and 2 g. of barium iodide (or 25 ml. of a 50 per cent. aqueous solution of potassium iodide) are put into a stoppered bottle, and the air is displaced by carbon disulphide. The bottle is heated in boiling water for 2 minutes. It is then shaken for 2 minutes, replaced in boiling water for 2 minutes, and again shaken. The hot liquid is then poured into 150 ml. of cold water, and the liberated iodine determined by titration with sodium thiosulphate solution.

*Hydroxy fatty acids* are insoluble in petroleum ether, whilst ordinary fatty acids are soluble : 5 g. of the oil is saponified by heating with excess of alcoholic caustic potash under a reflux condenser. The mixture is then evaporated to dryness on a water-bath. The residue is dissolved in water, washed into a separating-funnel, and acidified with hydrochloric acid. Petroleum ether is now added, and the separating-funnel shaken well and then allowed to stand for the petroleum ether to separate. Hydroxy fatty acids if present will form a brown flocculent layer between the aqueous layer and the petroleum ether.

**Oils used for Textile Purposes.**—*Olive Oil.*—The highest grade of olive oil is obtained by pressing ripe olives at atmospheric temperature, without breaking the kernels. This is used for medicinal purposes. The residue is broken up, mixed with hot water, and pressed again. This gives second-quality oil, used for salad oil and high-grade soap. The residue from the second pressing is ground, mixed with boiling water, and pressed, after which the residue is extracted with carbon disulphide. The oil obtained is used chiefly for textile soaps. Olive oil consists largely of triolein. It contains

also about 7 per cent. of linolic acid,  $C_{17}H_{33}.COOH$ , and a little arachidic acid,  $C_{19}H_{39}.COOH$ . The titer of the fatty acid is from  $17^{\circ}$  to  $25^{\circ}$  C.

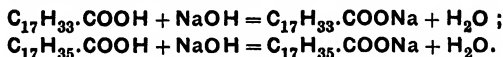
*Arachis Oil.*—This is obtained from the peanut, which contains about 45 per cent. of oil. It is extracted in the same way as olive oil. The properties of arachis oil are similar to those of olive oil, except that it contains about 5 per cent. of arachidic acid and has a higher titer ( $28^{\circ}$  to  $29^{\circ}$  C.). It is used for making textile soaps and also for yarn-lubricating emulsions.

*Neatsfoot Oil.*—This is a pale yellow liquid oil obtained from the hoofs of animals. It contains a considerable proportion of oleic acid. It has good lubricating properties, and is used for the preparation of yarn lubricants. It is occasionally adulterated with cotton-seed oil, which is objectionable for textile purposes. This oil can be detected by the Halphen test: To 3 ml. of the oil are added 1 ml. of a 2 per cent. solution of sulphur in carbon disulphide and 1 ml. of amyl alcohol. The mixture is then heated in boiling water. In the presence of cotton-seed oil a rose-red colour will be produced.

### Soaps.

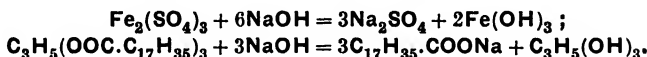
The term *soap* is applied, in general, to the metallic salts of the higher fatty acids and of oleic acid, and in particular to the sodium and potassium compounds, which are soluble in water.

Soaps may be prepared by neutralizing fatty acids with the hydroxide or carbonate of sodium or potassium. Thus oleic and stearic acids, when neutralized with sodium hydroxide, give respectively

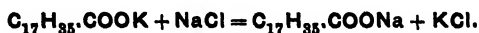


A great deal of soap is made in this way from commercial fatty acids, obtained either from recovered grease, or by the decomposition of fats by enzymes or other catalytic agents. As a rule, however, it is prepared from the fats by decomposing, or saponifying, them with caustic soda or potash.

The fats used in the manufacture of soap consist chiefly of triglycerides. When a glyceride is boiled with a solution of caustic soda or potash, it is decomposed in the same way as an inorganic salt, the sodium or potassium salt of the acid and the hydroxide of the base being produced. This is illustrated by the equations:

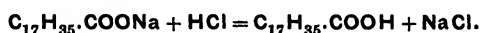


Thus, when a triglyceride is decomposed with sodium or potassium hydroxide (i.e. saponified), a soap and glycerol are formed. The sodium soaps are the common *hard* soaps, the corresponding potassium compounds being termed *soft* soaps. Both are soluble in hot water. The sodium soaps are separated from the glycerol by taking advantage of the fact that they are insoluble in strong salt solutions. If the mixture of soap and glycerol, obtained by saponification, is saturated with salt, the soap becomes insoluble, and rises to the surface owing to the greater specific gravity of the salt solution. It is then skimmed off, washed, cast into cakes, and dried. The brine is evaporated, and the glycerol removed by distillation under reduced pressure, the salt being recovered at the same time. If salt is added to a solution of a potassium soap, the latter is decomposed, potassium chloride and the sodium soap being formed, thus:



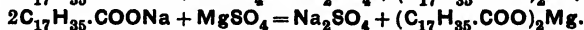
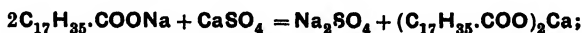
Hence, it is not possible to salt out a potassium soap by means of sodium chloride. The mixture of potash soap and glycerol is generally sold as such. Many potash soaps, however, made from fatty acids, do not contain glycerol. It is possible to obtain a hard potash soap if a hard fat, such as tallow, or its fatty acids be used, but it is always softer than the corresponding sodium compound. Soft potash soaps sometimes contain white specks known as *figs*. These consist, generally, of small pieces of potassium stearate, which is a fairly hard soap. They are produced by adding some tallow to the oil during saponification. Sodium carbonate and silicate are sometimes incorporated with soaps, either to increase their hardness or to improve their detergent properties.

**Properties of Soaps.**—Both sodium and potassium soaps are only sparingly soluble in cold, but readily soluble in hot, water. When a hot concentrated solution of a soap is cooled, the soap does not crystallize like an inorganic salt, but forms a jelly which melts again on warming. This property increases with the molecular weight of the fatty acid of the soap. In this property of forming a jelly, soap is similar to starch and glue, all being *colloids*; in fact, it owes its value in scouring largely to its colloidal properties. Soap dissolves in hot alcohol, but is only very sparingly soluble in other organic solvents, such as ether or petroleum ether. Benzene has, however, the power of dissolving certain soaps, particularly those of the heavy metals. Lead oleates are also soluble in ether. Solutions of soaps in benzene are used as detergents. Different soaps require different amounts of salt to cause their precipitation. Coconut- and palm-oil soaps require much more than others, and are, on this account, used in the manufacture of marine soaps, since they are capable of giving a lather with sea water. Soap is decomposed by acids with the liberation of the fatty acid:



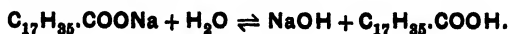
If hydrochloric acid is added to an aqueous solution of soap at a low temperature until the mixture turns methyl orange red, the whole of the fatty acid present will be liberated in the form of a white flaky precipitate. If the mixture is heated for some time in boiling water, the fatty acids melt and rise to the surface, forming a clear oily layer.

When a solution of soap is treated with a soluble metallic salt, whose soap is insoluble in water, this insoluble soap is immediately thrown down. In the case of calcium and magnesium sulphates the reactions are represented by the equations:



The production of insoluble calcium and magnesium soaps is the source of much trouble in scouring, bleaching, and dyeing. Zinc or aluminium soap is sometimes produced intentionally for the purpose of giving a fabric water-proof properties.

Although soap is neutral in its reaction in the dry form or when dissolved in alcohol, yet when dissolved in water or diluted spirit its solution is always alkaline. If a pure soap be dissolved in alcohol the solution gives no colour with phenolphthalein. But if excess of distilled water be added to a little of the solution a pink colour immediately appears, indicating the presence of an alkaline compound. This alkali is produced by hydrolysis, free fatty acid being liberated at the same time:



Different soaps are hydrolysed to different extents, depending upon the nature of the fatty acids they contain. As a general rule, the higher the molecular weight of the fatty acid the more readily does a soap become hydrolysed. The amount of alkali liberated by hydrolysis depends also upon the dilution and temperature of the solution, increasing with these up to a certain point. In the case of a particular soap solution of 10 g. per litre strength, the effect of dilution upon hydrolysis is seen in Table XXXI. It will be noted that

TABLE XXXI.—EFFECT OF DILUTION ON HYDROLYSIS OF SOAP.

Dilution.	0.1N. Acid required to neutralize Alkali liberated, ml.
1 in 20 . . . . .	1.2
1 „ 30 . . . . .	3.6
1 „ 40 . . . . .	4.0
1 „ 50 . . . . .	4.0

after a dilution of 1 in 40 was reached the further addition of water did not cause the liberation of any more alkali. The amount of hydrolysis in the case of sodium and potassium palmitates at 90° C. is shown in Table XXXII (reprinted from *Third Report on Colloidal Chemistry*, 1920, p. 5), the concentration of the soap solution being expressed in terms of normality. The increase of hydrolysis with increasing dilution is very marked. The products of hydrolysis are not necessarily so simple as represented in the equation given above, for the formation of both acid and basic soaps is possible.

TABLE XXXII.—HYDROLYSIS OF SODIUM AND POTASSIUM PALMITATES.

Normality of Soap Solution.	Percentage Hydrolysis of Sodium Palmitate.	Percentage Hydrolysis of Potassium Palmitate.
1.0	0.20	0.08
0.75	0.30	0.31
0.5	0.37	0.65
0.1	1.28	1.25
0.05	2.22	2.02
0.01	6.60	6.80

Hydrolysis of a soap solution is retarded by alkalis, glycerol, and neutral salts. If two equal weights of soap are placed in beakers, and one is dissolved in distilled water and the other in the same volume of a dilute solution of sodium chloride, it will be found that, after adding some phenolphthalein, less acid is required to discharge the pink colour in the beaker containing salt than in the other. When a certain proportion of salt is present, hydrolysis is entirely prevented, and no pink colour is produced with phenolphthalein.

When a solution of soap is shaken with distilled water, a foam or lather is produced. The lathering power of soaps can be compared by measuring the volume of a solution of each, of the same strength, necessary to give a foam

when shaken with a definite volume of distilled water in a stoppered bottle. The lathering power of a soap depends upon the fat from which it was prepared. As a rule, a soap which is freely soluble in water has a greater lathering power than a less soluble one, and one which hydrolyses readily gives more foam than one which does not.

The most important property of soap is its power of forming emulsions, particularly with oil. In an emulsion of oil in soap and water very minute particles of oil are distributed throughout the liquid, so finely divided that they do not readily coalesce and separate. The power which soap has of forming emulsions is due to its low interfacial tension with respect to oil. Nuttall (*J. Soc. Chem. Ind.*, 1920, **39**, 67r) describes this as follows:

"Firstly, the soap becomes concentrated at the surface of the oil globules, and owing to the surface viscosity produced thereby, the film of liquid intervening between two oil globules resists thinning and the consequent coalescence of the globules. If a fair-sized globule of thick mineral oil is placed on the surface of a somewhat concentrated solution of saponin and, by means of a pipette, saponin solution is introduced into the centre of the floating globule of oil, it is possible to produce a bubble of oil filled with saponin solution, the bubble itself floating within the external solution. The thin layer of oil forming the skin of the bubble, whilst of itself quite incapable of giving a tenacious film, has, under the conditions of the experiment, become so fortified both internally and externally by the saponin adsorbed at each interface that a comparatively rigid structure results. This bubble of oil is, in fact, a large-scale representation of the condition of a minute oil globule in an oil emulsion, except, of course, that in the latter case, the globule of oil contains none of the emulsifying agent within itself.

"The second reason why a liquid possessing a low interfacial tension with respect to oil should possess high emulsifying powers is as follows: The force tending to break the aqueous film intervening between the globules of oil is that of the interfacial

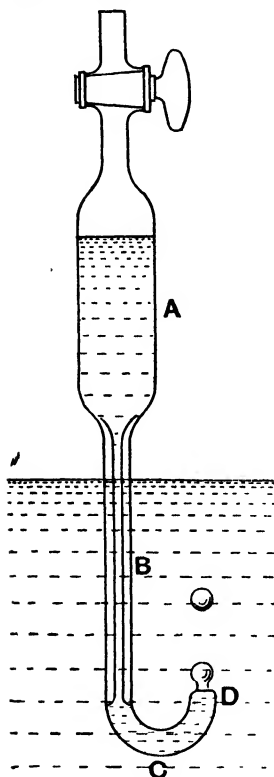


Fig. 109.—Drop-number Apparatus.

tension of the aqueous liquid to the oil, and if this is small it is not enough to withdraw the aqueous film separating the globules.

"Thus, the main requisite for a liquid to have a high emulsifying power towards an oil is, that it shall possess a low interfacial tension towards that oil. The main factor in determining wetting power is a low interfacial tension towards the surface to be wetted. Thus a good emulsifier is generally a good 'wetter,' and determination of emulsifying power a good indication of wetting power."

**Measurement of Emulsifying Power.**—The lowering of the surface tension, and hence the emulsifying power of a soap, may be studied by means of Donnan's apparatus for determining the *drop number*. The following description of this apparatus, shown in Fig. 109, is taken from Reiley and Rey's *Physical Methods*, 1, p. 526: "A pipette *A* of about 5 c.c. capacity is

provided with a capillary tube *B*, formed to a bend at *C*. This is drawn out to a point at *D*, which is ground off flat. The pipette is filled with an oil such as petroleum ether and the outlet *D* submerged in a solution of the soap. When the tap is open, the size of the drop which issues from *D* depends upon (1) the difference in specific gravity of the two liquids, which must be immiscible; and (2) the surface tension acting round the drop at the point *D*, which tends to retain the drops. Any decrease in surface tension shows itself, therefore, in diminished size and increased number of the drops. This increase is directly proportional to the emulsifying power of the soap solution. If the pipette is filled with paraffin oil or petroleum ether and immersed in water, only a small number of large drops will be formed from the 5 cc. in the pipette. If the water is now replaced by soap solution a great increase in the number of drops will be observed, accompanied by a corresponding decrease in their size. The relative emulsifying power of two or more soaps can be compared if standard conditions of experiment are maintained."

Shorter (*J. Soc. Chem. Ind.*, 1919, **38**, 249A) found that soap acts in two ways: firstly, by lowering the interfacial tension between the water and oil; and, secondly, by *stabilizing* the emulsion and suspensions. With soap solution and a mineral oil, the drop number increases rapidly with increasing concentration of the soap solution up to 0.4 per cent. of soap. Further increase in the strength of the soap solution has little effect on the drop number, *i.e.* there is no further increase of emulsifying power. This maximum concentration is not necessarily the same for all soaps, but with any soap it is wasteful to use a concentration above this maximum. The maximum stability of the emulsion is given with a soap solution of from 0.2 to 0.3 per cent. strength. Alkalis were found to increase the emulsifying power of a soap, but above a certain percentage to diminish the stability of the emulsion.

Closely related to the emulsification of oil is the power which soap solutions possess of forming colloidal solutions with mineral and organic bodies. If lamp-black is shaken with water, and the suspension passed through a filter-paper, it is separated completely by the filter, and a perfectly clear filtrate is obtained. If, however, the lamp-black is shaken with a solution of soap, it is adsorbed by the soap, and assumes a colloidal condition. If the mixture is now passed through a filter-paper, the filtrate is no longer clear. Some of the lamp-black passes through the paper with the soap solution. Other bodies, such as iron oxide or hydroxide and particles of dirt, form similar colloidal solutions. Spring (*J. Soc. Chem. Ind.*, 1909, **28**, 430; 1910, **29**, 99, 363) found that a 1 per cent. soap solution would carry 206 times as much clay and 37 times as much silica through a filter-paper as water alone.

**Detergent Action of Soap.**—Many theories have been brought forward to explain the detergent power of soap. The simplest and one of the older is that the action depends entirely upon hydrolysis, the cleansing action being due to saponification of grease by the liberated alkali, the solution of the soap so formed setting free the dirt. Although this may be one of the factors concerned, it cannot be considered as even the chief. The quantity of alkali liberated would be altogether too little for the purpose, nor would it have any saponifying action in so dilute a solution under the conditions used. Moreover, more alkali is liberated from dilute than from the more concentrated soap solutions which are actually used in practice. The carbon dioxide present in the water would also generally be sufficient to convert the hydroxide liberated by hydrolysis into sodium carbonate, which has very little saponifying action. But grease always contains some free fatty acids, which might be converted into soap by this alkali.

Another theory proposed by Jackson is founded on the phenomenon of the Brownian movement or pedesis. When finely-divided particles of insoluble matter are suspended in water and examined under the microscope, they are seen to be constantly oscillating in every direction. This is known as the *Brownian movement*. The presence of certain bodies, notably soap, increases the movement, just as others, such as salts, retard it. According to this theory of cleansing, the dissolved soap and alkali liberated by its hydrolysis first saponify or emulsify the grease which cements the particle of dirt to the fabric, and thus liberate the dirt. If this is sufficiently large, or is attached merely to the surface of the fabric, it is removed from the fabric by the force of gravity. But if the particles are minute and entangled in the fibres, gravity alone will not remove them. As soon as they are freed from their greasy envelope they commence oscillating, the rate of oscillation being accelerated by the dissolved soap, and thus become gradually freed from the fabric. Small quantities of alkalis, such as sodium hydroxide, carbonate, or silicate, act as assistants, while neutral salts, in general, and other bodies, such as glycerin, tend to inhibit the action.

The *colloidal-solution theory* is founded upon experiments similar to those of Spring described above. It depends upon the property which is possessed by colloids of forming adsorption compounds with various inorganic and organic bodies, which are not themselves of a colloidal nature. But the adsorption compounds are, at any rate temporarily, colloidal, and thus capable of forming colloidal solutions, and the colloidal theory suggests that dirt is removed in this way from textile fabrics when they are scoured with soap and water. The *emulsion theory* depends upon the property described above, which soap solutions possess, of emulsifying oils, fats, waxes, and even unsaponifiable oils. If a sufficiently stable emulsion be produced, the oils can be washed away, the particles of dirt and other solid bodies either remaining suspended in the liquor or forming adsorption compounds with the colloidal soap.

It is evident from the above summary of some of the theories that the detergent action of soap must depend on a number of factors. The *Third Report on Colloidal Chemistry*, 1920, expresses these as (i) the necessity of having the soap in solution; (ii) the power of emulsification, which goes parallel with low surface tension and the formation of surface-films; (iii) the wetting power, which, like the last, is ascribable to the undecomposed soap itself; (iv) the action of soap in forming non-adhesive colloidal adsorption compounds, with tissue and impurities, capable of remaining in stable suspension; and (v) it is essential that the soap should be in a colloidal form.

**Measurement of Detergent Power.**—The detergent power of a soap can be measured by the method of McBain, Harborne and King (*J. Soc. Chem. Ind.*, 1923, 42, 373r): 1 g. of "Auk" carbon-black is digested with 20 ml. of the soap solution at a constant temperature for 2 hours, and the mixture shaken and allowed to stand for an hour. It is then filtered at the temperature of digestion through a Whatman No. 31 filter-paper of 11.3 cm. diameter. Ten ml. of the filtrate is diluted to a known volume with alcohol, and the colour matched with a standard solution of a mixture of nigrosine and Bismarck brown.

**Rosin Soaps.**—When crude turpentine is distilled with steam, the residue after removal of the turpentine contains rosin. It is a yellow or brown transparent solid substance, which is very brittle and has a melting-point of from 70° to 140° C. When heated it burns with a yellow smoky flame and characteristic smell. It is insoluble in water, but dissolves readily in alcohol,

has an acid reaction, and can be neutralized with alkalis like the solution of a fatty acid. The chief constituent of this solution is abietic acid,  $C_{19}H_{29}COOH$ . This is a monobasic acid, which when neutralized with sodium or potassium hydroxide forms compounds having the properties of an ordinary soap. Rosin soaps may be made by boiling rosin with a solution of sodium hydroxide or a carbonate. Their solutions have marked detergent action. Like ordinary soaps, rosin soaps are decomposed by acids, with the liberation of the rosin acids. They give similar insoluble soaps with solutions of soluble salts of calcium and magnesium. Their solutions, like those of soap, emulsify oils and form adsorption compounds with dirt.

**Sulphonated Oils \* and Soaps.**—These bodies are very powerful emulsifiers, and are readily soluble in water. They are frequently termed *soluble oils*. Turkey-red oil, the most important of the sulphonated oils, is made from castor oil by the action of sulphuric acid. The concentrated acid is added gradually to the oil, with constant stirring, and keeping the temperature below  $35^{\circ}C$ ., till the product becomes completely soluble in water. If the temperature is allowed to rise above  $35^{\circ}C$ ., charring occurs and sulphur dioxide is formed. The composition of the product is not quite certain; the chief constituent is probably ricinosulphuric acid,  $C_{17}H_{32}(O.SO_2OH).COOH$ , whilst some free ricinoic acid,  $C_{17}H_{32}(OH).COOH$ , is also formed. After sufficient sulphuric acid has been added to the oil, the mixture is allowed to settle; the lower layer is drawn off, and the sulphonated oil is washed with a solution of sodium sulphate till it is only faintly acid. Caustic soda or ammonia is then added carefully till a sample emulsifies completely when shaken with a little water. The oil is not completely neutralized, and still gives an acid reaction. If sufficient alkali be added to neutralize the mixture completely, a sulphonated soap is obtained. Ricinosulphuric acid is soluble in water, and its aqueous solution gives a lather in the same way as a soap solution. It may be separated from turkey-red oil by shaking it with a mineral acid. An important property of turkey-red oil is that it can dissolve calcium salts, forming soluble calcium salts of ricinosulphuric acid. The oil or soap made from it does not give a precipitate with hard water as does ordinary soap. Turkey-red oil owes its name to its use in turkey-red dyeing. The soaps made by completely neutralizing sulphonated oils with sodium or potassium hydroxide are completely soluble in cold water, and are excellent emulsifying agents. These soaps enter into the composition of many proprietary articles, such as "Monopol," and other special soaps. Mixed with organic solvents they are used for the removal of oil and other stains from fabrics. They are also very useful, owing to their ready solubility, in assisting the penetration of dye and other liquors in the case of heavy goods, and may be used with advantage in nearly every case where the bath is either neutral or alkaline. Many "levelling" preparations are solutions of sulphonated soap and oleic acid in benzene or a similar solvent.

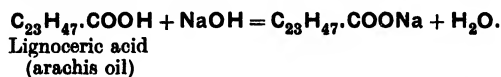
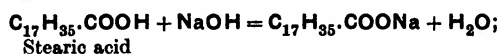
**Selection of Soaps.**—A good soap should fulfil the following conditions:—

(1) It should contain at least 62 per cent. of fatty acids, and from 6.5 to 8.5 per cent. of combined alkali expressed as sodium oxide,  $Na_2O$ . The quantity of combined alkali depends upon the molecular weight of the fatty acids present. The higher the molecular weight of these the lower will be the percentage of combined alkali. Since soaps made from fatty acids with a high molecular weight are, as a rule, better than those made from fatty acids with a low molecular weight, a low percentage of combined alkali is a good thing if the fatty acids are above 62 per cent. The relation between molecular weight

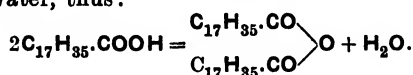
\* The term *sulphonated oils* is always used by dyers, although the compounds are generally sulphuric esters or their sodium salts.



of the fatty acid and combined alkali is seen from the following equations:—



The alkali is expressed as sodium oxide,  $\text{Na}_2\text{O}$ , since soap may be regarded as a compound of this body with the fatty anhydride. The anhydrides of the fatty acids are produced by the combination of two molecules of acid with the elimination of water, thus:



When the anhydride is saturated with a base, a soap is formed:



The proportion of fatty anhydrides can be obtained, very closely, by multiplying the percentage of fatty acids by 0.97. In a pure dry soap the sum of the fatty anhydrides and sodium oxide would be 100. In a good commercial soap this number should be from 70 to 72 per cent., the difference between this and 100 being water.

(2) Neither free fat, unsaponifiable oil, nor free (*i.e.* uncombined) alkali should be present. Free caustic alkali denotes careless manufacture, but sodium carbonate or silicate is often added purposely to impart hardness or to improve the detergent action of the soap. But it is always better to use a pure soap, and if necessary add alkali to the bath.

(3) Salts, such as sodium chloride or sulphate, should be present only in very small quantities, since they tend to inhibit the detergent action of a soap. Glycerol acts in the same way, but is rarely present in any quantity.

(4) The emulsifying power of the soap should be high when tested by the drop-number apparatus described above.

(5) Rosin should be absent from all textile soaps, since it is liable to cause loss of colour, particularly when hard water is used. It can be recognized by the following test: About 1 g. of the fatty acids prepared from the soap is dissolved in a little warm acetic anhydride. The solution is poured on to a white porcelain tile, and a drop of sulphuric acid placed near it and allowed to impinge on the edge of the acetic anhydride. The production of a violet colour indicates the presence of rosin.

(6) For scouring animal fibres and particularly wool, which cannot be scoured at a high temperature, the soap should have a low titer, not exceeding  $35^\circ\text{C}$ . On the other hand, a soap having a higher titer gives better results with cotton. The *titer* of a soap or oil is the temperature at which its fatty acids solidify. This is fairly constant for the same oil, and its determination gives some information about the oil used in the manufacture of the soap. The titers of some common oils and fats are

	$^\circ\text{C}$ .
Castor oil . . . . .	3.0
Olive oil . . . . .	17 to 25
Arachis oil . . . . .	29
Coconut oil . . . . .	29 to 30
Cotton-seed oil . . . . .	34 to 35
Bone fat . . . . .	38 to 40
Tallow . . . . .	40 to 45

In order to determine the titer, the dried fatty acids are poured into a dry test-tube, which should be about 6 cm. long and 3.5 cm. wide, and the fatty acids should half fill the tube. A delicate thermometer is then immersed in the liquid fatty acids, and the tube allowed to cool until a few crystals appear. The mass is then stirred with the thermometer without allowing it to touch the side of the tube, in such a way that the solidified portion is completely mixed with the rest of the fatty acid. The temperature will continue to fall for a time, but, finally, it will cease falling and rise suddenly a little, and then remain stationary for a short time as the fatty acid solidifies. This stationary temperature is the titer.

Table XXXIII gives the composition of a number of typical soaps.

TABLE XXXIII.—COMPOSITION OF TYPICAL SOAPS.

Sample.	Fatty Acids, per cent.	Un-saponified Fat, per cent.	Combined Alkali, per cent.	Free Alkali Carbonate, per cent.	Titer of Mixed Fatty Acids, ° C.	Remarks.
1. Mottled soap .	64.06	0.25	8.50	0.50	42	} Good soaps.
2. White curd .	62.00	0.25	7.50	0.25	35	
3. Olein .	65.24	Trace	7.59	Trace	16.5	
4. Vegetable oil .	64.62	0.10	7.64	0.15	24	
5. Olein and tallow	62.88	0.20	7.00	Trace	18.7	
6. Soft soap .	44.46	..	9.45	..	12	Good soft soap.
7. Olein (poor quality)	61.93	2.09	7.76	0.27	..	} Poor textile soaps.
8. Tallow .	58.75	1.07	6.61	0.28	..	
9. „ .	59.67	..	7.75	3.25	..	
10. Powder .	85.00	0.25	11.30	0.30	..	Good powder.
11. „ .	51.42	..	6.31	33.18	..	Poor powder.

**Types of Soap.**—The following are some of the commoner types of scouring soaps:—

**Mottled Soap.**—This is very commonly made from bone grease, the mottling being due to some of the lye remaining in the interstices of the curd, the impurities which it contains causing the colour. Blue and grey mottled soaps are coloured by means of ultramarine and manganese dioxide. In addition to bone fat, vegetable oils, such as cotton-seed oil, are used, and sometimes rosin. Soaps made from cotton-seed or soya oil are apt to leave a smell if hard water be used, and lime soaps become fixed in the fabric. In a well-made mottled soap the percentage of foreign insoluble matter is never very high, since it settles down as the soaps cool, instead of remaining in them. But the addition of such bodies as sodium silicate prevents the rapid settling of dirt, etc., and thus sometimes gives a soap a somewhat false appearance. Thus, while a good mottled soap always contains 63 per cent. of fatty acids, it can be made quite firm and apparently as good, and yet only contain 57 to 58 per cent.

**Curd Soaps.**—These are largely made from tallow, with or without the addition of a vegetable oil, such as coconut oil. They contain, as a rule, less fatty acid than mottled soaps, the content frequently falling to 60 per cent. The percentage of combined alkali should be small, i.e. from 6.5 to 7 per cent., and free alkali should be entirely absent. A little silica is sometimes present.

**Oil Soaps.**—These are generally brown in colour, and are made from olein

or recovered grease. In the latter case they often contain considerable quantities of unsaponifiable matter. A pure olein soap is the best that can be obtained for practically all textile purposes, owing to its ready solubility and high detergent power. It should always be examined for unsaponified or unsaponifiable matter.

*Vegetable-oil Soaps.*—This name is given to soaps made from a mixture of vegetable oils with a low titer like that of olein. They are, therefore, somewhat similar to olein soaps. Olive-oil soap is unsurpassable, but it is often adulterated with arachis and other oils. It sometimes consists entirely of foreign oils coloured to simulate olive oil.

*Dried or Desiccated Soaps.*—These consist of partly or completely dried soap. Flaked soap contains about 70 per cent. of fatty acids, while in desiccated soap powders the fatty-acid content may be considerably higher. Soap powders are sometimes mixed with such substances as sodium carbonate or borax, which reduce their value. They should always be bought upon their fatty-acid content. If the use of sodium carbonate is desirable, it is better to add it separately, rather than buy it at the price of soap. The variable nature of soap powders may be seen from the analyses of commercial samples given in Table XXXIV.

TABLE XXXIV.—COMPOSITION OF COMMERCIAL SOAP POWDERS.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Fatty acids . . .	78.90	44.80	30.40	66.15	62.09	52.91	28.83	53.20	7.01
Total alkali . . .	..	20.30	18.50	..	..	..	..	..	..
Combined alkali . .	9.11	..	..	7.98	7.07	7.47	1.80	7.53	0.70
Free sodium carbonate	3.64	..	..	2.50	17.19	18.45	57.52	11.86	69.65
Sodium silicate . . .	..	..	..	..	..	..	10.87	..	10.46

*Soft Soaps.*—These are made from either fatty acids or oil, potash being substituted for soda in the saponification. When made from an oil no attempt is made to remove the glycerol, which remains and helps to give the soap its characteristic appearance. Rosin is sometimes added. Potash soaps are always better than the corresponding soda soaps for scouring purposes, those containing no glycerol being best. They contain 45 per cent. of fatty acids.

*Textile Soaps.*—For wool-scouring a neutral olive-oil soap is the most suitable. Free alkali, sodium silicate, rosin, and unsaponified or unsaponifiable fat should be absent. Free alkali injures the fibre; silicate gives it a harsh feel; rosin forms sticky, insoluble soaps if calcium or magnesium is present, which cannot be removed; while free oil detracts from the emulsifying power of the soap, and also may be adsorbed and retained by the fibres.

On account of the high cost of olive-oil soap, olein or vegetable-oil soaps are commonly used in its place, or even curd soaps. But whatever soap is used, it must be freely soluble in water at the temperature of the scouring-bath. For scouring silk, also, no soap can compare with neutral potash olive-oil soap, and ready solubility at the temperature of the bath is an essential condition. In the scouring of cotton, less readily soluble soaps may be employed, since a higher temperature is used. Moreover, traces of free alkali have no deleterious action on the cotton fibre.

### Wetting Agents.

A wetting agent is a chemical which is used to assist the penetration of scouring, dyeing, or other liquors used in a textile process. Soap is a wetting agent, but the term is generally reserved for more specialized products. They may act directly or indirectly. Organic solvents such as toluene and pyridine act indirectly by dissolving grease, and thus facilitating penetration. But true wetting agents act by decreasing interfacial tension.

When a drop of liquid is placed upon the surface of a solid, either it may assume a spherical form, and neither spread over the solid surface nor wet it, or it may become flattened or spread out uniformly over the surface. In either of the last two cases it will probably wet the surface over which it has spread. Spreading power is essential to wetting, though not necessarily the same thing as wetting power. The spreading power is determined by the angle of contact between the liquid and the solid. When the drop retains a hemispherical form, this will be  $90^\circ$ ; when it spreads out completely, the angle will be zero. Hence, for a liquid to have a high wetting power, the latter condition must be fulfilled. The chief factors which determine spreading and wetting power are (i) the surface tension of the liquid, (ii) the surface tension of the solid, and (iii) the interfacial tension between the liquid and the solid.

According to Nuttall (*J. Soc. Chem. Ind.*, 1920, **39**, 67T), the first of these  $T_1$  will be exerted in the direction of the arrows at  $A$  (Fig. 110), and will tend to maintain the drop in a partly spherical form.

The interfacial tension  $T_{1.s}$  will act in the direction of the arrows at  $B$ , and will tend to roll up the drop, maintaining its spherical form. The surface tension of the solid  $T_s$  is exerted in the direction of the arrows at  $C$ , and its effect will be to draw out the drop into a lenticular form, the angle of contact  $\theta$  becoming smaller, until finally, when the drop forms a continuous film on the surface of the solid, it is reduced to zero. In order that this may occur,  $T_s$  must be greater than the sum of  $T_1$  and  $T_{1.s}$ , i.e.  $\{T_s - (T_1 + T_{1.s})\}$  must be positive. If it be negative, there can be no wetting action. In order that a liquid may have a high wetting power for a solid, it is evident that it must have a low surface tension  $T_1$  and a low interfacial tension  $T_{1.s}$ . The effect of reducing  $T_{1.s}$  will be to cause the liquid to spread over the surface of the solid, even if the surface tension  $T_1$  is fairly high. Thus the interfacial tension  $T_{1.s}$  becomes the chief factor in wetting.

Edser (*Brit. Ass. Colloid Rep.*, 1922, **11**, 293) expresses this relationship in the following manner:—

$$\cos \theta = \frac{T_s - T_{1.s}}{T_1}.$$

For perfect wetting  $\theta$  must be zero, so that

$$\frac{T_s - T_{1.s}}{T_1} = \cos 0^\circ = 1;$$

i.e.

$$T_s - T_{1.s} = T_1.$$

This means that wetting is possible only when the difference between the surface tension of the solid and the tension of the liquid-solid interface is equal to or greater than the surface tension of the liquid. If  $T_1 > T_s - T_{1.s}$ , then

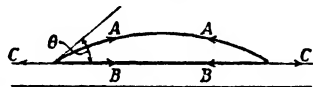


Fig. 110.

$\cos \theta < 1$ , and the contact angle is between  $0^\circ$  and  $90^\circ$ . In this case, in order to produce wetting, either  $T_s$  must be increased, or  $T_1$  or  $T_{1,s}$  decreased.

It should be noted that  $T_s$  and  $T_{1,s}$  cannot easily be determined experimentally. Although  $T_1$  can be measured, it does not give all the information required. Hence the best method of testing is to carry out trial experiments under the exact conditions of the operation for which the sample will be used. Some of the factors to be considered are concentration, pH, and temperature. According to M. Stiller (*J. Soc. Dyers Col.*, 1935, 51, 232), the following method for determining the surface tension of a wetting agent gives reliable results:

The apparatus consists of a 25- to 50-ml. wide-necked bottle, fitted with a two-holed cork, one hole carrying a capillary tube and the other a right-angled tube attached to a bellows. A thin steel scale, graduated in 0.5 mm., is fitted through the cork behind the capillary tube, and the pointed end, which projects below the cork, is protected against corrosion by platinizing or nickel-plating. The calibrated capillary tube is cleaned with warm chromic and sulphuric acids, rinsed well with distilled water, then with a few millilitres of dilute alcohol, next with 5 to 10 ml. of absolute ethyl alcohol, and finally with 5 to 10 ml. of pure ether. The last traces of ether are removed by attaching to the pump. The capillary tube is inserted in the cork so that, with the latter in position, the end of the tube is about 3 to 5 mm. above the surface of the liquid. The right-angled tube comes only 5 to 8 mm. below the cork. The bottle is filled to one-third to one-half of its volume with the solution, the cork inserted, and the capillary carefully adjusted so that the end is about 3 mm. below the surface of the liquid and perpendicular to it. If the surface tension is to be measured against the vapour pressure of the liquid itself, a little time must elapse, with the right-angled tube closed, to ensure that the vapour has penetrated the capillary tube. The end of the measuring scale is carefully adjusted so that the tip just touches the surface of the liquid, and the latter is forced up the dry capillary tube about 10 mm. above the level determined for water, by applying gradual pressure from the bellows. When a wet capillary tube is used, it is first rinsed out with the solution and adjusted as above, but the liquid is forced up to the top of the tube, and any drops at the top are removed with a clean filter-paper. As the liquid drops back, inclusion of air bubbles must be avoided. When there is no further drop in the meniscus on releasing the pressure, the height  $h$  in mm. of the solution in the capillary tube is noted, as well as the temperatures of the room and liquid. The surface tension in dynes per centimetre is calculated from the equation

$$\gamma = \frac{r h s}{2} \times 9.81,$$

where  $r$  is the diameter of the capillary in mm., and  $s$  the specific gravity of the solution at the temperature of the experiment. This procedure is recommended, in particular, for comparing the efficiencies of wetting agents and textile assistants in practice.

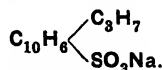
Cooper and Nuttall (*Analyst*, 1915, 40, 463) recommend the following method: Some of the liquid is weighed in a weighing-bottle. A piece of glass tubing coated externally and internally with collodion is dipped into the liquid and withdrawn. The bottle is then reweighed. The difference between the two weights, giving the weight of liquid adhering to the tube, gives a measure of its wetting power.

In practical wetting tests a piece of the material is floated on the surface of the solution of the wetting agent, and the time taken to sink beneath the

surface noted; or the weight of liquid which it takes up in a definite time is determined.

The constitution of wetting agents is very varied. Soap and turkey-red oil are the best known. Others include the following:—

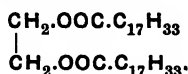
(1) Substitution products of naphthalene-sulphonic acids, such as Nekal B and Permal W, which have the constitution



(2) Esterified sulphonated fatty acids, *e.g.* Avirol AH,  $\text{C}_{17}\text{H}_{33}(\text{O}.\text{SO}_2.\text{ONa})$ .  $\text{COOC}_4\text{H}_9$ .

(3) Sulphonated fatty alcohols,\* *e.g.* Brilliant Avirol, sodium cetylsulphate,  $\text{C}_{16}\text{H}_{33}.\text{O}.\text{SO}_2.\text{ONa}$ .

(4) Esterified glycols, *e.g.* glycol dioleate,



(5) Sulphonated lauryl alcohol, *lauro*l,  $\text{C}_{12}\text{H}_{25}.\text{O}.\text{SO}_2.\text{ONa}$ .

(6) Sulphonated oleyl alcohol, *ocen*ol,  $\text{C}_{18}\text{H}_{35}.\text{O}.\text{SO}_2.\text{ONa}$ .

(7) Sodium salt of the compound of oleic acid with taurine, Ipegon T,  $\text{C}_{17}\text{H}_{33}.\text{CO}.\text{NH}.\text{(CH}_2)_2.\text{SO}_3\text{Na}$ .

### Waterproofing Agents.

A waterproofed fabric may act in two ways: It may show an increased interfacial tension, thus causing a drop of water placed upon it to assume a globular form; or the water may spread over the surface of the fabric, but be unable to penetrate it. In the latter case the exposed surface is wetted, but the inner surface remains dry. These two effects are distinct from each other, and if they can be produced simultaneously, perfect waterproofing results. The surface tension of the treated material may be judged approximately by placing a drop of water on it and observing whether it forms a globule or spreads over the surface. The resistance to penetration may be inferred by (i) the flotation method and (ii) the immersion method.

In the flotation method a small circular piece of the material is placed on the surface of water, and the following points are noted: (a) the time taken for the surface to become wet, and (b) the time taken for the pattern to sink beneath the surface of the water.

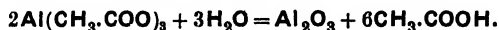
In the immersion method a standard piece of the material is immersed in water for a given time, and its handle noted. It is then exposed to air, and the time required to dry is observed. Alternatively, it may be weighed, and the percentage of retained water calculated.

If the fabric is woven (*i.e.* has no loops), the following method may be used: A burette is cut off above the tap, and the end ground flat. The lower end is covered with a piece of the material held in position by a rubber band. The burette is then suspended vertically, and water is dropped into it from a second burette until it begins to run through the fabric. The height of the column of water in the first burette is then measured.

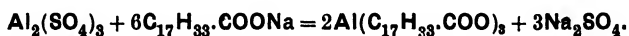
The principal waterproofing agents are (i) fats and waxes, (ii) metallic oxides, (iii) metallic soaps, and (iv) rubber. Of these rubber is in a different category from the others, being used principally to produce finishes impervious

\* See footnote on p. 199.

to air. The chief waxes are ceresine, Japan wax, stearin, paraffin wax, and montan wax, whilst metallic oxides include those of aluminium and tin. Aluminium oxide may be formed in the fabric by treating it with a solution of aluminium acetate, followed by drying and steaming; the following change takes place:—



Other metallic oxides are precipitated in the fabric by treating it with a salt of the metal and then with ammonia solution or sodium hydroxide. Metallic soaps are obtained by interaction of sodium soap with a soluble salt of the metal. Thus, the material may be soaked in a solution of aluminium sulphate, squeezed, and passed into an aqueous solution of soap, when the following change occurs:—



A single-bath process may be used also. In this case the aluminium sulphate and soap are dissolved separately, and mixed in a colloid mill together with a little emulsifying agent such as lauroyl. The goods are then padded with this mixture, squeezed, and dried. The authors (*J. Soc. Chem. Ind.*, 1938, 57, 56) investigated the waterproofing properties of a number of substances both separately and together. Ceresine was found to be the most efficient of the waxes, and aluminium oxide the best oxide. The stearates of aluminium and chromium are the most efficient of the soaps, followed by those of strontium, titanium, and tin. The following process was found to give good results with hosiery goods: The goods are first treated with a mixture of 5 g. of ceresine emulsified in 100 ml. of 2 per cent. potassium stearate solution. Without rinsing they are then transferred to a cold bath containing aluminium acetate solution (sp. gr. 1.030), after which they are squeezed, and dried at a temperature of 230° F. (110° C.).

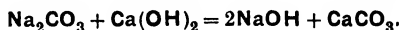
*Velan PF* is a cation active water-repelling substance which has been produced by I.C.I. during recent years. The term "cation active" implies that the substance, when dissolved in water, gives a complex organic ion bearing a positive charge. Since most textile fibres are negatively charged in the presence of water they possess an affinity for the positively-charged ion. Conversely, "anion active" substances dissociate with the formation of complex ions bearing a negative charge.

In the application of velan, the material is immersed in a solution containing 1 to 4 per cent. of Velan PF on the weight of the goods and some sodium acetate. After hydro-extraction, the goods are dried and heated to between 100° and 150° F. for about five minutes. This is followed by a rinse in soap and thorough removal of any residual soap with clean water. The water-repellent finish obtained in this way is permanent and is not affected by subsequent washing. Velan PF also gives the material a soft handle, and the product is frequently used as a softening agent only, in which case the heating after drying is not necessary.

## CHAPTER XVI.

### ALKALIS AND ACIDS.

**Caustic Soda, Sodium Hydroxide, NaOH.**—This is made by the Leblanc process or by the electrolysis of an aqueous solution of common salt. In the former, a hot or boiling solution of sodium carbonate is treated with lime, which decomposes the carbonate in accordance with the equation:



When an aqueous solution of salt is electrolysed, chlorine and sodium are first formed. The sodium which is liberated at the cathode decomposes the water present, giving sodium hydroxide and hydrogen, whilst the chlorine liberated at the anode is collected, or used for the preparation of either hydrochloric acid or a hypochlorite.

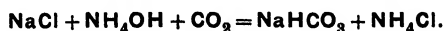
Sodium hydroxide is a white, solid, highly caustic substance. It is very deliquescent, becoming liquid rapidly when exposed to air. It is readily soluble in water, and heat is developed during its dissolution. When preparing an aqueous solution, the hydroxide should be added slowly to the water with constant stirring, or the solid substance may be placed in a suitable vessel, which is suspended beneath the surface of the water. When exposed to air, sodium hydroxide and its aqueous solutions absorb and combine with carbon dioxide. Like other so-called caustic substances, it attacks the skin and other animal tissues.

Commercial caustic soda may have the form of lumps, sticks, or powder. It is generally sold on the basis of its content of sodium oxide,  $\text{Na}_2\text{O}$ . The chief impurities are the carbonate, chloride, and sulphate of sodium.

**Caustic Potash, Potassium Hydroxide, KOH.**—This is made in the same way as sodium hydroxide, and has similar properties.

The strengths of solutions of caustic alkalis for textile purposes are commonly tested by taking their specific gravity with a hydrometer and referring to Table XXXV, p. 208.

**Sodium Carbonate,  $\text{Na}_2\text{CO}_3$ .**—This is prepared in several ways. In the Solvay process a concentrated solution of salt is mixed with ammonia, and subjected to the action of a stream of carbon dioxide, when ammonium chloride and sodium bicarbonate are formed in accordance with the equation:



The sodium bicarbonate is much less soluble than the ammonium chloride, and crystallizes out. It is collected, dried, and heated, when the following change takes place:—





TABLE XXXV.—SPECIFIC GRAVITIES OF SOLUTIONS OF SODIUM AND POTASSIUM HYDROXIDES AT 15°/4° C.

Sp. gr.	NaOH, per cent.	KOH, per cent.	Sp. gr.	NaOH, per cent.	KOH, per cent.	Sp. gr.	NaOH, per cent.	KOH, per cent.
1.010	0.86	1.18	1.190	16.91	20.17	1.370	33.73	37.37
1.020	1.69	2.28	1.200	17.81	21.17	1.380	34.71	38.28
1.030	2.60	3.36	1.210	18.71	22.16	1.390	35.68	39.18
1.040	3.50	4.44	1.220	19.65	23.17	1.400	36.67	40.09
1.050	4.34	5.53	1.230	20.60	24.14	1.410	37.65	40.98
1.060	5.20	6.60	1.240	21.47	25.13	1.420	38.67	41.87
1.070	6.13	7.68	1.250	22.33	26.10	1.430	39.67	42.76
1.080	7.05	8.76	1.260	23.23	27.07	1.440	40.68	43.63
1.090	7.95	9.82	1.270	24.13	28.04	1.450	41.70	44.50
1.100	8.78	10.87	1.280	25.04	29.00	1.460	42.75	45.37
1.110	9.67	11.92	1.290	25.96	29.96	1.470	43.80	46.23
1.120	10.56	12.96	1.300	26.85	30.91	1.480	44.85	47.09
1.130	11.55	14.01	1.310	27.85	31.84	1.490	45.89	47.93
1.140	12.49	15.04	1.320	28.83	32.78	1.500	46.94	48.78
1.150	13.34	16.08	1.330	29.80	33.70	1.510	48.00	49.64
1.160	14.19	17.10	1.340	30.74	34.63	1.520	49.05	50.48
1.170	15.06	18.13	1.350	31.75	35.55	1.530	50.10	51.32
1.180	16.00	19.15	1.360	32.79	36.46	..	..	..

Sodium carbonate is a colourless, crystalline compound. Its maximum solubility in water is at 32.5° C., at which temperature 100 parts of water dissolve 31.6 of the salt. Sodium carbonate crystallizes from water in large crystals having the composition  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . These constitute ordinary *soda* or *washing soda*. When exposed to air, they gradually *effloresce*, that is, give up a part of the water of crystallization, becoming coated with a compound,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , termed *crystal soda*. If exposed for a sufficient time, the whole crystal gradually crumbles to a powder. When crystallized from hot solutions, the crystals are represented by the formula  $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ . When a solution of sodium bicarbonate,  $\text{NaHCO}_3$ , is boiled, it is gradually changed into sodium carbonate, carbon dioxide being given off:



If the temperature of the solution is regulated, only a part of the bicarbonate is decomposed, and if the solution is then cooled, crystals of the composition  $\text{Na}_2\text{CO}_3 \cdot 2\text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$  are deposited. This product is known as *sodium sesquicarbonate*. It is found in Africa and South America as a natural deposit. The commercial forms of sodium carbonate naturally contain different percentages of sodium carbonate according to the amount of water of crystallization which they contain. Table XXXVI shows the composition of some commercial samples.

An aqueous solution of sodium carbonate has an alkaline reaction, owing to the fact that sodium hydroxide is liberated by hydrolysis:

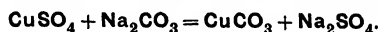


Compared with an equivalent solution of sodium hydroxide, sodium carbonate is a comparatively "mild" alkali; that is, the concentration of hydroxyl ions is less. It can be used in many operations for which sodium hydroxide

TABLE XXXVI.—COMPOSITION OF COMMERCIAL SAMPLES OF SODIUM CARBONATE.

	48- per cent. Na <sub>2</sub> O.	58- per cent. Na <sub>2</sub> O.	Pure Ammonia Alkali.	Soda Crystals.	Crystal Soda.	Sesqui- carbonate.
Sodium carbonate .	60.64	98.72	98.94	34.22	81.92	46.62
Sodium bicarbonate .	..	..	..	..	..	37.30
Sodium sulphate .	4.35	0.20	0.20	2.54	0.18	..
Sodium hydroxide .	1.29	..	..	0.10	..	..
Sodium chloride .	28.34	0.54	0.36	0.27	0.24	0.29
Ferric oxide .	Trace	0.04	..	..	..	..
Alumina .	1.12	0.01	..	..	..	..
Silica .	0.00	0.09	0.09	0.03	..	..
Water .	4.26	0.26	0.38	62.84	17.66	15.79

would be inadmissible. Solutions of salts of heavy metals generally give precipitates of insoluble carbonates when treated with sodium carbonate; *e.g.*

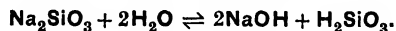


**Sodium Bicarbonate, NaHCO<sub>3</sub>.**—This is a white crystalline substance, less soluble in water than sodium carbonate. When its aqueous solutions are heated, the bicarbonate is decomposed, thus:

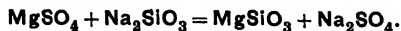


A cold aqueous solution of sodium bicarbonate acts as a weak acid, since it contains replaceable hydrogen. It decomposes calcium hypochlorite with liberation of hypochlorous acid, and neutralizes bases.

**Sodium Silicates.**—These are derived from either orthosilicic acid, H<sub>4</sub>SiO<sub>4</sub>, or metasilicic acid, H<sub>2</sub>SiO<sub>3</sub>. The sodium and potassium salts of these are soluble in water, but other silicates are insoluble. Sodium metasilicate, Na<sub>2</sub>SiO<sub>3</sub>, and water-glass, Na<sub>2</sub>SiO<sub>3</sub>·3SiO<sub>2</sub>, when dissolved in water undergo hydrolysis, with liberation of sodium hydroxide:



Aqueous solutions of silicates have also colloidal properties. They are used in textile processes as mild alkalis, as stabilizers in the case of bleaching with hydrogen peroxide, and as detergents in combination with soap. Aqueous solutions of sodium silicate give insoluble silicates of other metals when added to solutions of their salts, thus:



Sodium silicate is used, for this reason, in the weighting of silk.

**Borax, Sodium Tetraborate, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O.**—This compound is found in Nature, or is made by neutralizing a hot aqueous solution of boric acid with sodium carbonate and allowing it to crystallize:



Borax is a white crystalline substance, sparingly soluble in water. Its aqueous solution has an alkaline reaction owing to hydrolysis, and is used as a mild alkali. Metallic borates are used also in the fireproofing of textile fabrics.

**Ammonia,  $\text{NH}_3$ .**—On the industrial scale ammonia is made from *ammoniacal liquor*, which is a by-product in the manufacture of coal-gas. This consists of a solution in water of ammonia and ammonium salts. When it is boiled with milk of lime, the free ammonia is expelled, and the ammonium salts are decomposed. The liberated ammonia is passed through solutions of lime and caustic soda to remove the impurities present, such as sulphides, pyridine, and tar oils. It is then passed through charcoal to purify it further, and ultimately led either into sulphuric acid to form ammonium sulphate or into water if pure ammonia liquor is required. The usual strength of ammonia liquor is about 36 per cent. of ammonia,  $\text{NH}_3$ , corresponding to a specific gravity of 0.880; this is known as *ammonium fortissimum*. A somewhat lower strength, namely 28 per cent., with a specific gravity of 0.900, is also made.

TABLE XXXVII.—SPECIFIC GRAVITIES OF AQUEOUS AMMONIA AT 15° C.  
(Lunge and Wiernik.)

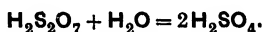
Specific Gravity at 15° C.	Per cent. $\text{NH}_3$ by Weight.	1 Litre contains Grams $\text{NH}_3$ .	Correction of the Specific Gravity for +1° C.	Specific Gravity at 15° C.	Per cent. $\text{NH}_3$ by Weight.	1 Litre contains Grams $\text{NH}_3$ .	Correction of the Specific Gravity for +1° C.
1.000	0.00	0.0	0.00018	0.940	15.63	146.9	0.00039
0.998	0.45	4.5	0.00018	0.938	16.22	152.1	0.00040
0.996	0.91	9.1	0.00019	0.936	16.82	157.4	0.00041
0.994	1.37	13.6	0.00019	0.934	17.42	162.7	0.00041
0.992	1.84	18.2	0.00020	0.932	18.03	168.1	0.00042
0.990	2.31	22.9	0.00020	0.930	18.64	173.4	0.00042
0.988	2.80	27.7	0.00021	0.928	19.25	178.6	0.00043
0.986	3.30	32.5	0.00021	0.926	19.87	184.2	0.00044
0.984	3.80	37.4	0.00022	0.924	20.49	189.3	0.00045
0.982	4.30	42.2	0.00022	0.922	21.12	194.7	0.00046
0.980	4.80	47.0	0.00023	0.920	21.75	200.1	0.00047
0.978	5.30	51.8	0.00023	0.918	22.39	205.6	0.00048
0.976	5.80	56.6	0.00024	0.916	23.03	210.9	0.00049
0.974	6.30	61.4	0.00024	0.914	23.68	216.3	0.00050
0.972	6.80	66.1	0.00025	0.912	24.33	221.9	0.00051
0.970	7.31	70.9	0.00025	0.910	24.99	227.4	0.00052
0.968	7.82	75.7	0.00026	0.908	25.65	232.9	0.00053
0.966	8.33	80.5	0.00026	0.906	26.31	238.3	0.00054
0.964	8.84	85.2	0.00027	0.904	26.98	243.9	0.00055
0.962	9.35	89.9	0.00028	0.902	27.65	249.4	0.00056
0.960	9.91	95.1	0.00029	0.900	28.33	255.0	0.00057
0.958	10.47	100.3	0.00030	0.898	29.01	260.5	0.00058
0.956	11.03	105.4	0.00031	0.896	29.69	266.0	0.00059
0.954	11.60	110.7	0.00032	0.894	30.37	271.5	0.00060
0.952	12.17	115.9	0.00033	0.892	31.05	277.0	0.00060
0.950	12.74	121.0	0.00034	0.890	31.75	282.6	0.00061
0.948	13.31	126.2	0.00035	0.888	32.50	288.6	0.00062
0.946	13.88	131.3	0.00036	0.886	33.25	294.6	0.00063
0.944	14.46	136.5	0.00037	0.884	34.10	301.4	0.00064
0.942	15.04	141.7	0.00038	0.882	34.95	308.3	0.00065

Ammonia is easily liquefied, and is very soluble in water. In all its reactions an aqueous solution of ammonia behaves as though it contained the compound  $\text{NH}_4\text{OH}$ , or *ammonium hydroxide*, in which the group  $-\text{NH}_4$  acts as a monovalent metal. The aqueous solution has an alkaline reaction, but is a "weak" alkali, and can be used in many textile operations for which a "strong" alkali would be inadmissible. When the aqueous solution is neutralized with an acid, ammonium salts are formed. These generally dissociate when dissolved in water, especially when their solutions are heated. Ammonium acetate,  $\text{CH}_3\text{COONH}_4$ , is used in dyeing for this reason, since when its aqueous solution is boiled, acetic acid is gradually liberated in accordance with the equation:



Ammonium hydroxide solution gives precipitates of metallic hydroxides with salts of heavy metals, some of which dissolve in excess of the reagent. Ammonium salts of common acids are volatilized by heat, and are used in the fireproofing of textile materials, since when volatilized they displace air. When evaporated to dryness, ammonia solution should give only traces of solid residue. The percentage of ammonia present may be ascertained by taking its specific gravity and referring to the table of corresponding strengths (Table XXXVII).

**Sulphuric Acid,  $\text{H}_2\text{SO}_4$ .**—Sulphur dioxide made by roasting pyrites in air is oxidized to sulphur trioxide,  $\text{SO}_3$ , when it is passed over platinized asbestos together with air at a temperature of  $430^\circ \text{C}$ . The sulphur trioxide is absorbed by pure sulphuric acid, giving pyrosulphuric acid or fuming sulphuric acid,  $\text{H}_2\text{S}_2\text{O}_7$ . When this is diluted cautiously with water, sulphuric acid is produced:



Sulphuric acid is an oily liquid having a specific gravity of 1.84. It absorbs water when exposed to air, and when mixed with water evolves heat. On cooling the hot solution, it is found that a contraction in volume has taken place, which is greatest when the proportions of acid and water correspond to the formula  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ . Sulphuric acid is a "strong" acid, *i.e.* its aqueous solutions have a high hydrogen-ion concentration, or a low *pH*-value. It gives rise to many metallic salts which are of importance in dyeing. The chief of these are

Sodium sulphate . . . .	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Magnesium sulphate . . . .	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Zinc sulphate . . . .	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
Ferrous sulphate . . . .	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Copper (cupric) sulphate . . . .	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Aluminium sulphate . . . .	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$
Chromium (chromic) sulphate . . . .	$\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

The specific gravity of aqueous solutions of sulphuric acid is given in Table XXXVIII.

**Hydrochloric Acid,  $\text{HCl}$ .**—Hydrochloric acid is a solution of gaseous hydrogen chloride in water, containing about 30 per cent.  $\text{HCl}$  by weight. This solution fumes when exposed to moist air. The gas can be made by treating salt with sulphuric acid, or by decomposing a solution of salt with an electric current and combining the chlorine obtained with the hydrogen which is simultaneously liberated. Hydrochloric acid is a "strong" acid. Its

TABLE XXXVIII.—SPECIFIC-GRAVITY DATA FOR SULPHURIC ACID.

Bé.	Sp. gr.	T <sub>w</sub> °	Per cent. H <sub>2</sub> SO <sub>4</sub>	Weight of 1 cu. ft. in lbs. Av.	Per cent. O. V.	Pounds O. V. in 1 cu. ft.	* Freezing (Melting) Point.	APPROXIMATE BOILING-POINTS.			
								50° Bé. 295° F.	145-6° O.		
0	1.0000	0.0	0.00	62.37	0.00	0.00	32.0° F.	60° " 386° "	196.7° "		
1	1.0069	1.4	1.02	62.30	1.09	0.68	31.2° "	61° " 400° "	204.4° "		
2	1.0140	2.8	2.08	62.24	2.23	1.41	30.5° "	62° " 415° "	212.8° "		
3	1.0211	4.2	3.13	62.09	3.36	2.14	29.8° "	63° " 432° "	222.3° "		
4	1.0284	5.7	4.21	64.14	4.52	2.90	28.9° "	64° " 451° "	232.3° "		
5	1.0357	7.1	5.28	64.00	5.67	3.66	28.1° "	65° " 485° "	251.7° "		
6	1.0432	8.6	6.37	65.06	6.84	4.45	27.2° "	66° " 538° "	281.9° "		
7	1.0507	10.1	7.45	65.53	7.99	5.24	26.3° "				
8	1.0584	11.7	8.55	66.01	9.17	6.06	25.1° "				
9	1.0662	13.2	9.66	66.50	10.37	6.89	24.0° "				
10	1.0741	14.8	10.77	66.99	11.56	7.74	22.8° "				
11	1.0821	16.4	11.89	67.49	12.76	8.61	21.5° "				
12	1.0902	18.0	13.01	68.00	13.98	9.49	20.0° "				
13	1.0985	19.7	14.13	68.51	15.16	10.39	18.3° "				
14	1.1069	21.4	15.25	69.04	16.36	11.30	16.6° "				
15	1.1154	23.1	16.38	69.57	17.53	12.23	14.7° "				
16	1.1240	24.8	17.51	70.10	18.81	13.19	12.6° "				
17	1.1328	26.6	18.73	70.65	20.08	14.18	10.2° "				
18	1.1417	28.3	19.89	71.21	21.84	15.20	7.7° "				
19	1.1508	30.2	21.07	71.78	22.61	16.23	4.8° "				
20	1.1600	32.0	22.25	72.35	23.87	17.27	1.8° "				
21	1.1694	33.9	23.43	72.94	25.14	18.34	- 1.3° "				
22	1.1789	35.8	24.61	73.53	26.41	19.42	- 6.0° "				
23	1.1885	37.7	25.81	74.13	27.69	20.53	- 11° "				
24	1.1983	39.7	27.03	74.74	29.00	21.68	- 16° "				
25	1.2083	41.7	28.28	75.36	30.34	22.87	- 23° "				
26	1.2185	43.7	29.53	76.00	31.69	24.08	- 30° "				
27	1.2288	45.8	30.79	76.64	33.04	25.32	- 39° "				
28	1.2393	47.9	32.05	77.30	34.39	26.58	- 49° "				
29	1.2500	50.0	33.33	77.96	35.76	27.88	- 61° "				
30	1.2609	52.2	34.63	78.64	37.16	29.22	- 74° "				
31	1.2719	54.4	35.98	79.33	38.55	30.68	- 82° "				
32	1.2832	56.6	37.26	80.03	39.98	32.00	- 96° "				
33	1.2946	58.9	38.68	80.74	41.40	33.42	- 97° "				
34	1.3063	61.3	39.92	81.47	42.83	34.90	- 91° "				
35	1.3182	63.6	41.27	82.22	44.28	36.41	- 81° "				
36	1.3303	66.1	42.63	82.97	45.74	37.95	- 70° "				
37	1.3426	68.5	43.99	83.74	47.20	39.53	- 60° "				
38	1.3551	71.0	45.35	84.52	48.66	41.13	- 53° "				
39	1.3679	73.6	46.72	85.32	50.13	42.77	- 47° "				
40	1.3810	76.2	48.10	86.13	51.61	44.45	- 41° "				
41	1.3942	78.8	49.47	86.96	53.08	46.16	- 35° "				
42	1.4078	81.6	50.87	87.80	54.58	47.92	- 31° "				
43	1.4216	84.3	52.26	88.67	56.07	49.72	- 27° "				
44	1.4356	87.1	53.66	89.54	57.58	51.56	- 23° "				
45	1.4500	90.0	55.07	90.44	59.09	53.44	- 20° "				
46	1.4646	92.9	56.48	91.35	60.60	55.36	- 14° "				
47	1.4796	95.9	57.90	92.23	62.13	57.33	- 15° "				
48	1.4948	99.0	59.32	93.23	63.65	59.34	- 18° "				
49	1.5104	102.1	60.75	94.20	65.18	61.40	- 22° "				
50	1.5268	105.3	62.18	95.20	66.72	63.52	- 27° "				
51	1.5426	108.6	63.66	96.21	68.31	65.72	- 33° "				
52	1.5591	111.8	65.13	97.24	69.89	67.96	- 39° "				
53	1.5761	115.2	66.63	98.30	71.50	70.23	- 49° "				
54	1.5934	118.7	68.13	99.33	73.11	72.68	- 59° "				
55	1.6111	122.2	69.65	100.48	74.74	75.10	- 70° "				
56	1.6292	125.8	71.17	101.61	76.37	77.60	- 82° "				
57	1.6477	129.5	72.75	102.77	78.07	80.23	- 96° "				
58	1.6667	133.3	74.36	103.96	79.79	82.95	- 112° "				
59	1.6860	137.2	75.99	105.16	81.54	85.75	- 126° "				
60	1.7059	141.2	77.67	106.40	83.35	88.63	- 142° "				
61	1.7262	145.2	79.43	107.66	85.23	91.76	- 158° "				
62	1.7470	149.4	81.30	108.96	87.24	95.06	- 174° "				
63	1.7683	153.7	83.24	110.29	89.43	98.63	- 191° "				
64	1.7901	158.0	85.06	111.65	91.92	102.63	- 208° "				
64.1	1.7957	159.1	86.38	112.00	92.64	103.75	- 214° "				
64.2	1.8012	160.2	87.04	112.34	93.40	104.03	- 219° "				
64.3	1.8068	161.4	87.81	112.69	94.23	104.19	- 224° "				
65	1.8125	162.5	88.56	113.05	95.13	107.54	- 229° "				
65.1	1.8182	163.6	89.55	113.40	96.10	108.97	- 234° "				
65.2	1.8239	164.8	90.80	113.76	97.23	110.60	- 239° "				
65.3	1.8297	165.9	91.80	114.12	98.51	112.42	- 244° "				
66	1.8354	167.1	92.19	114.47	100.00	114.47	- 249° "				

Sp. gr.	Per cent. H <sub>2</sub> SO <sub>4</sub>	Sp. gr.	Per cent. H <sub>2</sub> SO <sub>4</sub>
1.0000	0.00	1.5281	62.34
1.0043	0.71	1.5440	63.79
1.0047	5.14	1.5748	66.51
1.0049	9.48	1.6272	71.00
1.0092	14.22	1.6679	74.46
1.1035	19.04	1.7044	77.54
1.1736	23.94	1.7258	79.40
1.2105	28.55	1.7472	81.32
1.2513	33.49	1.7700	83.47
1.2951	38.64	1.7959	86.86
1.3441	44.15	1.8117	88.53
1.3947	49.52	1.8194	89.76
1.4307	53.17	1.8275	91.32
1.4667	56.68	1.8354	93.19
1.4822	58.14		

CORRECTIONS FOR 1° C.  
(Add when above 15° C., subtract when below 15° C.)

Sp. Gr.	Correction
1.170 (or less)	0.0006
1.170 to 1.450	0.0007
1.450 " 1.580	0.0008
1.580 " 1.750	0.0009
1.750 " 1.840	0.0010

Per cent. 60°	Pounds 60° in 1 cu. ft.	Per cent. 50°	Pounds 50° in 1 cu. ft.
61.93	53.34	77.36	66.63
63.69	55.39	79.56	69.19
65.50	57.50	81.81	71.58
67.28	59.66	84.05	74.53
69.09	61.86	86.30	77.27
70.90	64.12	88.56	80.10
72.72	66.43	90.83	82.98
74.55	68.79	93.12	85.93
76.37	71.20	95.40	88.94
78.22	73.68	97.70	92.03
80.06	76.21	100.00	95.20
81.96	78.85	102.38	98.50
83.86	81.54	104.74	101.85
85.79	84.33	107.15	105.33
87.72	87.17	109.57	108.89
89.67	90.10	112.01	112.56
91.63	93.11	114.46	116.30
93.67	96.26	117.00	120.24
95.74	99.52	119.69	124.31
97.84	102.89	122.21	128.52
100.00	106.40	124.91	132.91
102.27	110.10	127.74	137.52
104.67	114.05	130.75	142.47
107.30	118.24	134.08	147.82
110.29	122.14	137.76	153.81
111.15	124.49	138.84	155.50
112.06	126.89	139.98	157.25
113.05	129.03	141.22	159.14
114.14	130.75	142.67	161.17
115.80	132.70	144.02	163.53
116.65	134.88	145.71	165.76
118.19	138.88	147.68	168.48
119.98	143.84	149.87	171.56

Oil of Vitriol.

H<sub>2</sub>SO<sub>4</sub>.

Oil of Vitriol.

60°

66°

93.19

100.00

119.68

60°

77.67

88.55

108.00

50°

62.13

66.72

80.06

Acids stronger than 66° Bé. should have their percentage compositions determined by chemical analysis.

\* Calculated from Pickering's results (*J. Chem. Soc.*, 1890, 57, 363).

TABLE XXXIX.—SPECIFIC-GRAVITY DATA FOR HYDROCHLORIC ACID.

Bé.°	Sp. gr.	Tw.°	%HCL	Bé.°	Sp. gr.	Tw.°	%HCL	Bé.°	Sp. gr.	Tw.°	%HCL
1.00	1.0069	1.38	1.40	16.0	1.1240	24.80	24.57	20.8	1.1675	33.50	32.93
2.00	1.0140	2.80	2.82	16.1	1.1248	24.96	24.73	20.9	1.1684	33.68	33.12
3.00	1.0211	4.22	4.25	16.2	1.1256	25.12	24.90	21.0	1.1694	33.88	33.31
4.00	1.0284	5.68	5.69	16.3	1.1265	25.30	25.06	21.1	1.1703	34.06	33.50
5.00	1.0357	7.14	7.15	16.4	1.1274	25.48	25.23	21.2	1.1713	34.26	33.69
5.25	1.0375	7.50	7.52	16.5	1.1283	25.66	25.39	21.3	1.1722	34.44	33.88
5.50	1.0394	7.88	7.89	16.6	1.1292	25.84	25.56	21.4	1.1732	34.64	34.07
5.75	1.0413	8.26	8.26	16.7	1.1301	26.02	25.72	21.5	1.1741	34.82	34.26
6.00	1.0432	8.64	8.64	16.8	1.1310	26.20	25.89	21.6	1.1751	35.02	34.45
6.25	1.0450	9.00	9.02	16.9	1.1319	26.38	26.05	21.7	1.1760	35.20	34.64
6.50	1.0469	9.38	9.40	17.0	1.1328	26.56	26.22	21.8	1.1770	35.40	34.83
6.75	1.0488	9.76	9.78	17.1	1.1336	26.72	26.39	21.9	1.1779	35.58	35.02
7.00	1.0507	10.14	10.17	17.2	1.1345	26.90	26.56	22.0	1.1789	35.78	35.21
7.25	1.0526	10.52	10.55	17.3	1.1354	27.08	26.73	22.1	1.1798	35.96	35.40
7.50	1.0545	10.90	10.94	17.4	1.1363	27.26	26.90	22.2	1.1808	36.16	35.59
7.75	1.0564	11.28	11.32	17.5	1.1372	27.44	27.07	22.3	1.1817	36.34	35.78
8.00	1.0584	11.68	11.71	17.6	1.1381	27.62	27.24	22.4	1.1827	36.54	35.97
8.25	1.0603	12.06	12.09	17.7	1.1390	27.80	27.41	22.5	1.1836	36.72	36.16
8.50	1.0623	12.46	12.48	17.8	1.1399	27.98	27.58	22.6	1.1846	36.92	36.35
8.75	1.0642	12.84	12.87	17.9	1.1408	28.16	27.75	22.7	1.1856	37.12	36.54
9.00	1.0662	13.24	13.26	18.0	1.1417	28.34	27.92	22.8	1.1866	37.32	36.73
9.25	1.0681	13.62	13.65	18.1	1.1426	28.52	28.09	22.9	1.1875	37.50	36.93
9.50	1.0701	14.02	14.04	18.2	1.1435	28.70	28.26	23.0	1.1885	37.70	37.14
9.75	1.0721	14.42	14.43	18.3	1.1444	28.88	28.44	23.1	1.1895	37.90	37.36
10.00	1.0741	14.82	14.83	18.4	1.1453	29.06	28.61	23.2	1.1904	38.08	37.58
10.25	1.0761	15.22	15.22	18.5	1.1462	29.24	28.78	23.3	1.1914	38.28	37.80
10.50	1.0781	15.62	15.62	18.6	1.1471	29.42	28.95	23.4	1.1924	38.48	38.03
10.75	1.0801	16.02	16.01	18.7	1.1480	29.60	29.13	23.5	1.1934	38.68	38.26
11.00	1.0821	16.42	16.41	18.8	1.1489	29.78	29.30	23.6	1.1944	38.88	38.49
11.25	1.0841	16.82	16.81	18.9	1.1498	29.96	29.48	23.7	1.1953	39.06	38.72
11.50	1.0861	17.22	17.21	19.0	1.1508	30.16	29.65	23.8	1.1963	39.26	38.95
11.75	1.0881	17.62	17.61	19.1	1.1517	30.34	29.83	23.9	1.1973	39.46	39.18
12.00	1.0902	18.04	18.01	19.2	1.1526	30.52	30.00	24.0	1.1983	39.66	39.41
12.25	1.0922	18.44	18.41	19.3	1.1535	30.70	30.18	24.1	1.1993	39.86	39.64
12.50	1.0943	18.86	18.82	19.4	1.1544	30.88	30.35	24.2	1.2003	40.06	39.86
12.75	1.0964	19.28	19.22	19.5	1.1554	31.08	30.53	24.3	1.2013	40.26	40.09
13.00	1.0985	19.70	19.63	19.6	1.1563	31.26	30.71	24.4	1.2023	40.46	40.32
13.25	1.1006	20.12	20.04	19.7	1.1571	31.44	30.90	24.5	1.2033	40.66	40.55
13.50	1.1027	20.54	20.45	19.8	1.1581	31.62	31.08	24.6	1.2043	40.86	40.78
13.75	1.1048	20.96	20.86	19.9	1.1590	31.80	31.27	24.7	1.2053	41.06	41.01
14.00	1.1069	21.38	21.27	20.0	1.1600	32.00	31.45	24.8	1.2063	41.26	41.24
14.25	1.1090	21.80	21.68	20.1	1.1609	32.18	31.64	24.9	1.2073	41.46	41.48
14.50	1.1111	22.22	22.09	20.2	1.1619	32.38	31.82	25.0	1.2083	41.66	41.72
14.75	1.1132	22.64	22.60	20.3	1.1628	32.56	32.01	25.1	1.2093	41.86	41.99
15.00	1.1154	23.08	22.92	20.4	1.1637	32.74	32.19	25.2	1.2103	42.06	42.30
15.25	1.1176	23.52	23.33	20.5	1.1647	32.94	32.38	25.3	1.2114	42.28	42.64
15.50	1.1197	23.94	23.75	20.6	1.1656	33.12	32.56	25.4	1.2124	42.48	43.01
15.75	1.1219	24.38	24.16	20.7	1.1666	33.32	32.75	25.5	1.2134	42.68	43.40

## ALLOWANCE FOR TEMPERATURE.

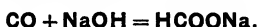
10°-15° Bé. . . . 1/40° Bé. or 0.0002 sp. gr. for 1° F.  
 15°-22° Bé. . . . 1/30° Bé. or 0.0003 " " 1° F.  
 20°-25° Bé. . . . 1/28° Bé. or 0.00035 " " 1° F.

tendering action on textile fibres has already been referred to. It forms many salts which have important textile applications. Among these are

Sodium chloride . . . . .	NaCl
Magnesium chloride . . . . .	MgCl <sub>2</sub>
Stannous chloride . . . . .	SnCl <sub>2</sub>
Stannic chloride . . . . .	SnCl <sub>4</sub>
Titanous chloride . . . . .	TiCl <sub>3</sub>

Table XXXIX gives the specific gravity of aqueous solutions of the acid.

**Formic Acid, H.CO.OH.**—This is a colourless, volatile liquid, made by distilling a mixture of oxalic acid and glycerin, or by passing carbon monoxide under pressure over soda-lime or caustic soda at a temperature of 210° C., when the following reaction takes place:—



The sodium formate is then decomposed with sulphuric acid and the formic acid removed by distillation. It is soluble in water. The aqueous solution is used as an assistant in dyeing wool, and as a reducing agent when mordanting wool with chromium.

**Acetic Acid, C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> or CH<sub>3</sub>.COOH.**—This is prepared by the dry distillation of wood or paper. When made in this way it is termed *pyroligneous acid*. It is also produced by the fermentation of a dilute solution of alcohol, as in the manufacture of vinegar, and by oxidation of acetaldehyde produced by the action of sulphuric acid on acetylene. Acetic acid is a colourless liquid which boils at 119° C. It crystallizes at 16.7° C., forming an ice-like mass known as *glacial acetic acid*. When water is added to glacial acetic acid, heat is evolved, followed by a contraction in volume when the solution cools. The greatest contraction corresponds to the formula C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>.H<sub>2</sub>O. The acid is soluble in water in all proportions.

Acetic acid is used in dyeing union goods or silk with acid dyestuffs. It has a lower hydrogen-ion concentration than formic acid, and therefore a correspondingly lower tendering effect on cotton. It is used in other dyeing processes also, for example with basic dyestuffs. On account of its small tendering action it can be employed to remove traces of alkali from cotton. When silk is soaked in a dilute solution of acetic acid, squeezed, and dried, it acquires a peculiar feel and power of rustling when squeezed, termed *scroop*. Acetic acid is monobasic. Its salts, the acetates, are prepared from it either by treating the acid with a metal or by neutralizing it with the oxide or carbonate. Some of the acetates are of importance in dyeing, e.g.:

Ferrous acetate, (CH <sub>3</sub> .COO) <sub>2</sub> Fe . . .	For weighting silk.
Calcium acetate, (CH <sub>3</sub> .COO) <sub>2</sub> Ca . . .	Assistant in dyeing with mordant dyestuffs.
Ammonium acetate, CH <sub>3</sub> .COONH <sub>4</sub> . . .	Assistant in dyeing.
Aluminium acetate, (CH <sub>3</sub> .COO) <sub>3</sub> Al . . .	Mordant for wool, and for waterproofing fabrics.

**Oxalic Acid, C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> or (COOH)<sub>2</sub>.**—Oxalic acid occurs in many plants, such as rhubarb. It is made by oxidizing sugar or cellulose with nitric acid and crystallizing out the solution. On a large scale it is made by heating sawdust with sodium hydroxide at about 240° C., when sodium oxalate is formed. This is dissolved in water and treated with lime. The precipitated calcium oxalate is then decomposed with sulphuric acid. It is a colourless substance,

which crystallizes with two molecules of water. The acid is dibasic, forming both acid and neutral salts. It is readily oxidized, and is used in dyeing as a reducing agent. Ferric oxalate is soluble in a solution of oxalic acid or acid potassium oxalate,  $\text{COOK.COOH}$ , and iron stains may be removed from fabrics by treating them with oxalic acid.

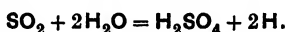
**Tartaric Acid**,  $\text{C}_4\text{H}_6\text{O}_6$  or  $\text{HOOC.CH(OH).CH(OH).COOH}$ .—This is a colourless, crystalline body, which is obtained in the wine industry from grape-juice. It is a dibasic acid, readily soluble in water. It is used for imparting scroop to silk. *Cream of tartar*, potassium hydrogen tartrate, is used as a reducing agent in mordanting wool; and *tartar emetic*, potassium antimonyl tartrate,  $\text{K.SbO.C}_4\text{H}_6\text{O}_6$ , for fixing tannic acid in the mordanting of cotton.



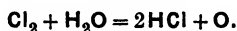
## CHAPTER XVII.

### BLEACHING AGENTS.

MUCH of the colouring matter of textile fabrics is removed with the impurities by scouring. There are, nevertheless, residual natural colouring matters which cannot be removed in this way. These bodies are, however, capable of being changed into colourless leuco compounds by means of nascent hydrogen, or oxidized into simpler soluble colourless compounds by nascent oxygen. The chemicals made use of for these purposes are termed *bleaching agents*. They are divided into two classes: (1) reducing bleaching agents, which bleach by producing nascent hydrogen; and (2) oxidizing bleaching agents, which give nascent oxygen either directly or indirectly. Reducing bleaching agents, such as sulphur dioxide, act in many cases by decomposing water with the liberation of hydrogen:



On the other hand, chlorine, an oxidizing bleaching agent, decomposes water and sets free the oxygen:



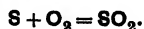
Nascent oxygen decomposes colouring matters, completely, into simpler compounds, which can be washed away with water, and which do not recombine to form the original colouring matter. Nascent hydrogen, on the contrary, does not always do this, but sometimes combines with the colouring matter, forming a colourless compound, which remains in the fabric, and which is gradually oxidized to the original colouring matter upon exposure to air. The white produced by reducing bleaching agents is not permanent, becoming yellow or brown upon exposure to air. That given by oxidizing bleaching agents does not, as a rule, become yellow. The choice of a bleaching agent is governed by the nature of the fibre, the degree of bleaching required, and the cost of the process. The chief bleaching agents are—

(1) *Reducing bleaching agents*: sulphur dioxide or sulphurous acid, sulphites or bisulphites, hydrosulphites.

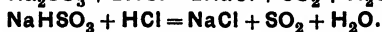
(2) *Oxidizing bleaching agents*: chlorine, hypochlorous acid or its salts, peroxides, persulphates, perborates, permanganates, and ozone.

#### Reducing Bleaching Agents.

**Sulphur dioxide,  $\text{SO}_2$ ,** is prepared commercially by roasting pyrites or by burning sulphur with excess of air:

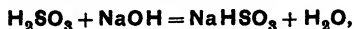


It is produced also when a sulphite or a bisulphite is treated with hydrochloric or sulphuric acid:



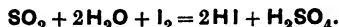


*Acidimetric titration* of sulphurous acid is difficult because it generally contains sulphuric acid, and it is not very sensitive to indicators. The normal sodium sulphite is alkaline to phenolphthalein, but sodium bisulphite,  $\text{NaHSO}_3$ , is acid to phenolphthalein and neutral to methyl orange. If methyl orange is used as the indicator, the equation is



and each ml. of decinormal sodium hydroxide used corresponds to 0.0064 gm.  $\text{SO}_2$ .

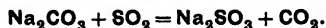
*Titration with iodine* is a more accurate method. This depends upon the reaction:



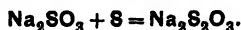
The solution of sulphurous acid is placed in a burette, and run into 25 ml. of decinormal iodine solution till the colour due to iodine just disappears. A drop or two of starch solution may be added as an indicator. As long as any iodine is present, the solution will be blue owing to the presence of iodide of starch. The starch solution should not be added till the iodine colour is nearly discharged. Each millilitre of decinormal iodine solution used corresponds to 0.0032 g. of sulphur dioxide,  $\text{SO}_2$ .

*Gravimetric method.* For very accurate determinations a gravimetric process should be employed. A known volume of the solution is run into excess of bromine-water. This oxidizes the sulphur dioxide to sulphuric acid. A few drops of hydrochloric acid are added, and the solution is boiled till all the bromine is expelled. Barium chloride is then added, which precipitates the sulphuric acid as barium sulphate. After boiling again for about five minutes the barium sulphate is filtered off, washed, ignited, and weighed. The weight of barium sulphate multiplied by 0.2747 gives sulphur dioxide.

**Sodium sulphite**,  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , is a colourless crystalline substance, readily soluble in water. It is made by passing sulphur dioxide into sodium carbonate solution till no more carbon dioxide is given off. The solution is then concentrated in the absence of air, and crystallized:

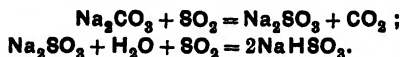


As stated above, when treated with hydrochloric or sulphuric acid, it is decomposed with the formation of sulphur dioxide. A solution of sodium sulphite,  $\text{Na}_2\text{SO}_3$ , has an alkaline reaction to litmus, phenolphthalein, and methyl orange. If the solid substance or its solution is exposed to air, it is oxidized gradually to sodium sulphate,  $\text{Na}_2\text{SO}_4$ . When a solution of sodium sulphite is heated with finely divided sulphur, the sulphur is dissolved, and sodium thiosulphate is formed:



Sodium sulphite is used as a solvent for sulphur in the dye-bath when dyeing with sulphur dyestuffs.

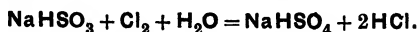
**Sodium bisulphite**,  $\text{NaHSO}_3$ , is obtained when excess of sulphur dioxide is passed into a cold saturated solution of sodium carbonate or a cold strong solution of sodium hydroxide:



When sodium bisulphite is dissolved in water, the solution acts as though it contained free sulphurous acid, produced by the reaction:



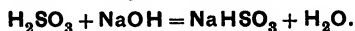
A dilute aqueous solution of the bisulphite is used in bleaching. It is also used as an antichlor in the chlorination of wool:



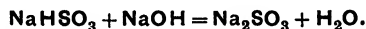
Sodium bisulphite is oxidized to bisulphate when exposed to air, and since it is hygroscopic, it deteriorates rapidly unless kept dry and in closed vessels. Sulphates can be detected by the formation of a white precipitate of barium sulphate, insoluble in hydrochloric acid, upon addition of barium chloride. Barium sulphite dissolves in hydrochloric acid, giving sulphur dioxide:



*Analysis of Sulphites: Estimation of Free Sulphurous Acid in the Presence of Bisulphite.*—Bisulphites are neutral to methyl orange and acid to phenolphthalein. This fact may be taken advantage of in the following way: To a measured quantity of the solution to be analysed a little of each indicator is added, and then decinormal caustic soda until the solution is neutral to methyl orange, when the free sulphurous acid will be present as sodium bisulphite, as shown by the following equation:

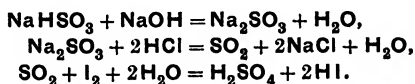


Having read the volume of caustic soda used, more is added until a faint pink colour is produced, which denotes that the whole of the sulphurous acid present has been converted into sodium sulphite in accordance with the equation:

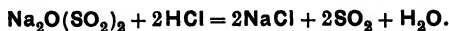


Each millilitre of alkali used in the first titration is equivalent to 0.0064 g. of  $\text{SO}_2$ , and from the first reading the amount of free sulphurous acid can be calculated, while the second will give the total amount of sulphur dioxide present as bisulphite. If the amount of free sulphurous acid calculated from the first reading be deducted from that given by the second, the percentage of bisulphite originally present can be calculated.

Mixtures of sodium sulphite and bisulphite can be analysed by a combination of the alkimetric and iodo methods based upon the equations:

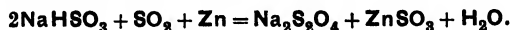


**Sodium metabisulphite**,  $\text{Na}_2\text{S}_2\text{O}_5$  or  $\text{Na}_2\text{O}(\text{SO}_2)_2$ , is a colourless crystalline salt containing 67.4 per cent. of sulphur dioxide, all of which can be liberated by means of acid:



It forms a very convenient source of sulphur dioxide.

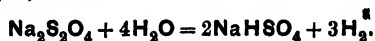
**Sodium hydrosulphite**,  $\text{Na}_2\text{S}_2\text{O}_4$ , is a stable white powder. It is prepared from sodium bisulphite by treatment with zinc dust and sulphurous acid in the proportions represented by the equation:



The zinc is precipitated by milk of lime, and the solution crystallized, when sodium hydrosulphite,  $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , is obtained.

Sodium hydrosulphite is a powerful reducing and bleaching agent. In

aqueous solution it decomposes water, becoming oxidized to sodium bisulphate and liberating hydrogen, thus:



The same reaction takes place when the substance is exposed to moist air, and the reducing action is developed either in neutral or in alkaline solutions. The fact that it will reduce in the presence of alkalis makes sodium hydrosulphite very useful in the preparation of indigo vats. It is also a powerful stripping agent for dyes. When treated with acids, it gives unstable hydrosulphurous acid, which breaks down into sulphur dioxide, sulphur, and water.

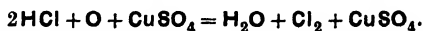
When treated with formaldehyde, a stable addition compound is produced having the composition  $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{CH}_2\text{O}$ . It is termed *sodium sulphyloxyate formaldehyde* or *decolein*. *Formosuls* are similar compounds, some of them being zinc salts. These compounds are soluble in water, but, unlike the hydrosulphites, their aqueous solutions have little reducing action. When treated with acids such as acetic, they are decomposed slowly on warming, with the formation of hydrosulphurous acid. Since the decomposition is complete only at the boiling-point, the reducing action can be developed very gradually. Decolein, zinc formosul, and similar compounds are powerful stripping agents.

### Oxidizing Bleaching Agents.

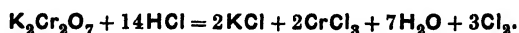
The most important of the oxidizing bleaching agents are chlorine and its compounds. Chlorine belongs to the group of elements known as the *halogens*. The family includes the following members:

	Atomic Weight.
Fluorine . . . . .	19.00
Chlorine . . . . .	35.457
Bromine . . . . .	79.916
Iodine . . . . .	126.92

**Chlorine.**—The commercial manufacture of chlorine is intimately connected with the Leblanc soda process, the first stage of which consists in treating salt with sulphuric acid, whereby sodium sulphate and hydrochloric acid are formed. This hydrochloric acid is either dissolved in water for the commercial acid, or converted into chlorine. The latter may be accomplished by means of manganese dioxide and sulphuric acid, or by the Deacon process. In the Deacon process the gaseous hydrochloric acid is mixed with air and passed over heated balls of pumice or clay saturated with a solution of copper sulphate or chloride, which acts as an oxygen-carrier, remaining unchanged at the end of the operation:

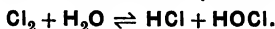


Chlorine is also prepared by the electrolysis of a solution of sodium chloride. In the laboratory it may be made by heating hydrochloric acid with potassium dichromate:

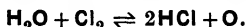


Chlorine is a greenish-yellow gas possessing a very pungent smell. When inhaled it attacks the mucous membrane of the nose, throat, and lungs, thus causing death by suffocation. It is readily liquefied by cooling it to  $-34^\circ \text{C}$ ., when it forms a yellow liquid which freezes at  $-102^\circ \text{C}$ . Liquid chlorine is now an article of commerce. Chlorine gas is 35.5 times as heavy as hydrogen, or 2.45 times as heavy as air. It is moderately soluble in water. One litre

of water at 0° C. dissolves 3.43 litres of the gas, and 3.00 litres at 17° C. If the aqueous solution be frozen, crystals of chlorine octahydrate,  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ , are formed. But when chlorine is dissolved in water, some of the water is decomposed with the formation of hypochlorous acid:



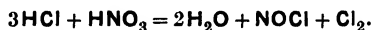
This reaction is reversible, and when the concentration of the chlorine exceeds 1 g. per litre, it goes back from right to left, so that free chlorine is again formed. If a solution of chlorine (chlorine-water) is kept for some time, a second reaction takes place, resulting in the formation of oxygen:



These changes are of importance in bleaching, and will be referred to again later.

Chlorine itself is not used much as a bleaching agent. Liquid chlorine may be made use of, however, in the preparation of bleaching solutions. These will be referred to later.

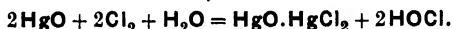
**Nitro-hydrochloric Acid, Aqua Regia**, which is used sometimes in the bleaching of silk, is a solution containing chlorine. It is prepared by mixing nitric acid and hydrochloric acid in the proportions represented by the equation:



The mixture is allowed to stand for two or three days, and is diluted before use to a density of 4° Tw.

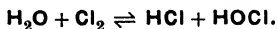
**Hypochlorous Acid, HOCl.**—This acid is formed by the combination of the acid oxide  $\text{Cl}_2\text{O}$  with water, though this method of preparation is only of theoretical interest. Hypochlorous acid may be made in the following ways:

(1) By passing chlorine into water containing freshly precipitated mercuric oxide in suspension:



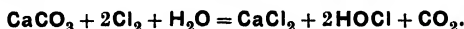
The excess of mercuric oxide and the double compound produced can be removed by filtration.

(2) When chlorine is passed into water, at first hypochlorous acid is produced:



But only very dilute solutions can be made, since the reaction is reversible, the hydrochloric acid being the controlling factor.

If finely powdered calcium carbonate is also present, the hydrochloric acid is neutralized as it is produced, and since hypochlorous acid is without action on calcium carbonate, much stronger solutions can now be obtained:



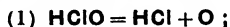
A similar reaction takes place in the presence of excess of sodium bicarbonate:



(3) Taylor and Bostock prepare hypochlorous acid by distilling a mixture of bleaching powder with thirty times its weight of water and twice its weight of boric acid. If 10 g. of bleaching powder, 300 ml. of water, and 20 g. of boric acid are used, the first 100 ml. distilled off may be regarded as practically pure hypochlorous acid and water.

*Properties.*—In dilute solutions hypochlorous acid is colourless, and has a characteristic smell. It is impossible to prepare concentrated solutions without decomposing the acid with the liberation of chlorine. Hence such solutions have the yellowish colour and smell of free chlorine.

A solution of hypochlorous acid is moderately stable if kept in the dark, but when exposed to light or warmed it decomposes rapidly. The changes which take place are rather complex, resulting in the formation of hydrochloric acid, chlorine, and oxygen, in accordance with the equations:



These reactions are brought about not only by the action of light, but also by catalytic agents such as metallic oxides, particularly those of iron, copper, and cobalt.

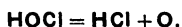
The presence of free chlorine in a solution of hypochlorous acid may be detected by the following test: Some of the liquid is shaken with excess of metallic mercury. In the presence of hypochlorous acid, a brownish-yellow precipitate of oxychloride of mercury,  $\text{HgO} \cdot \text{HgCl}_2$ , is produced. This precipitate is decomposed by dilute hydrochloric acid, giving soluble mercuric chloride,  $\text{HgCl}_2$ . When chlorine-water is shaken with metallic mercury, a white precipitate of mercurous chloride,  $\text{Hg}_2\text{Cl}_2$ , is formed, which does not dissolve when treated with hydrochloric acid.

Hypochlorous acid has only weak acid properties, and is monobasic. When neutralized with alkalis, it gives salts termed *hypochlorites*, which are decomposed by such weak acids as boric and carbonic:

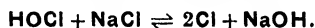


The hypochlorites of calcium and sodium are obtained, together with chlorides, by passing chlorine gas into an aqueous solution of the hydroxide.

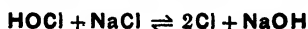
Both hypochlorous acid and the hypochlorites are used as bleaching agents. There is some difference of opinion as to the way in which hypochlorous acid acts, and, indeed, as to its power of bleaching. There are, in fact, two opposing views, which may be briefly discussed. Higgins and others think that hypochlorous acid has of itself bleaching properties, owing to the liberation of oxygen:



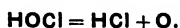
According to this view, the bleaching action is one of direct oxidation. On the other hand, Taylor believed that hypochlorous acid has only very feeble bleaching properties *per se*, only becoming active when nascent chlorine is liberated from it in accordance with the equations given above. In this connection it must be noted that the addition of sodium chloride to a solution of hypochlorous acid causes an increase in its bleaching power, which, however, is of only short duration. This is due probably to the reversible reaction:



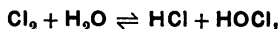
The addition of sodium chloride would cause this reaction to proceed in the  $\rightarrow$  direction till the sodium hydroxide produced is sufficient to set up a new equilibrium. This does not disprove the theory of Higgins, who admits that since chlorides are generally present in water, there is, no doubt, at first some nascent chlorine produced. The bleaching due to this ceases, however, as soon as the equilibrium corresponding to the reversible equation



is established, after which the action proceeds by reason of oxygen produced by the reaction:



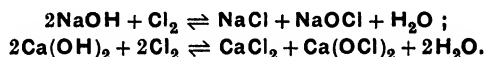
With solutions of hypochlorous acid, prepared by passing chlorine into water containing suspended calcium carbonate, there is a further difficulty which may be briefly referred to here. Higgins found that chlorine-water had only a feeble bleaching action on linen, but that if some calcium carbonate were added the bleaching power was greatly increased. He regarded this as being due to the neutralization of the hydrochloric acid produced by the equation:



which would allow more hypochlorous acid to be liberated. On the other hand, Taylor held that when calcium carbonate is added to either chlorine-water or hypochlorous acid prepared in other ways some calcium hypochlorite,  $\text{Ca}(\text{OCl})_2$ , is formed, and that this is the cause of the bleaching action observed, that is, calcium hypochlorite and not free hypochlorous acid is the bleaching agent, the calcium hypochlorite then liberating chlorine owing to the reversibility of the equation:



A solution of sodium, potassium, or calcium hypochlorite, together with chloride, may be made by passing chlorine into a cold solution of the hydroxide of the metal:

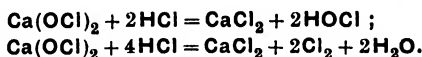


These reactions are reversible. If a hot solution of the hydroxide is used, chlorates are obtained:

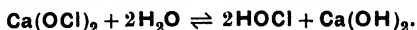


If a cold concentrated solution of sodium hydroxide is saturated with chlorine and evaporated at a low temperature, needle-shaped crystals of the composition  $\text{NaOCl} \cdot 6\text{H}_2\text{O}$  are obtained. Crystalline calcium hypochlorite,  $\text{Ca}(\text{OCl})_2 \cdot 4\text{H}_2\text{O}$ , is prepared in a similar manner.

Hypochlorites are generally soluble in water. They are decomposed by strong acids, either hypochlorous acid or chlorine being formed according to the quantity used:



Even such weak acids as boric and carbonic are able to decompose the hypochlorites, but in these cases the hypochlorous acid is not decomposed by excess. Another important property of the hypochlorites is that they are hydrolysed by water with liberation of hypochlorous acid:



This reaction is of considerable importance in connection with the bleaching of cotton, and will be referred to again later.

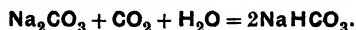
**Eau de Javelle.**—This name is applied to a solution of sodium hypochlorite prepared by passing chlorine into a solution of sodium carbonate. The reaction takes place in two stages, depending upon the quantity of chlorine



used. With one molecule of chlorine to one of sodium carbonate, sodium hypochlorite, sodium chloride, and carbon dioxide are formed:



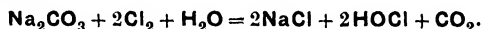
As long as any unchanged sodium carbonate is present, the carbon dioxide does not escape, but changes the sodium carbonate into sodium bicarbonate:



When no more sodium carbonate is left, the carbon dioxide begins to escape, causing effervescence. If the addition of chlorine is continued beyond this point, hypochlorous acid is formed:



Thus, if two molecules of chlorine are used for each molecule of sodium carbonate taken, we get

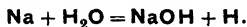


In order to obtain a stable solution, the introduction of chlorine must be stopped as soon as the evolution of carbon dioxide is noticeable, and the alkalinity of the solution restored by adding a little sodium carbonate. Acid solutions are unstable, and bleach too rapidly. Sodium hydroxide may be substituted for sodium carbonate, thus:



In this case, also, a little unchlorinated alkali must be left in solution to render the preparation stable.

**Preparation of Sodium Hypochlorite by Electrolysis of Salt.**—A solution of salt in water contains sodium and chlorine ions, which are continually in process of recombining and dissociating. They are charged equally and oppositely with negative and positive electricity, the chlorine ions being negative and the sodium ions positive. When an electric current is passed through the solution by immersing in the liquid two plates (or electrodes) connected by wires to the poles of a battery, the negatively charged ions, as they become dissociated, are directed towards the positive electrode (called the *anode*), while the positively charged ions travel towards the negative electrode (or *cathode*). As these ions reach the electrode their electric charge is neutralized by the opposite electricity of the electrode, and we no longer have ions, but chlorine and sodium atoms. The latter then decompose water and form sodium hydroxide:



Thus the final products are hydrogen, chlorine, and sodium hydroxide. If the two electrodes are separated from one another by a porous diaphragm, both chlorine and sodium hydroxide may be prepared in this way; but if the electrodes are near together, the chlorine comes into contact with the sodium hydroxide, and sodium hypochlorite is formed:



If only a single pair of electrodes is used, there is naturally a loss owing to the escape of some of the chlorine, but when a compound cell is employed, in which the salt solution passes successively between a series of electrodes arranged parallel to each other, the loss of chlorine is minimized. In this way concentrated solutions, containing as much as 35 g. of chlorine per litre, can

be produced. The successive arrangement of the electrodes is seen in Fig. 111. The salt solution (electrolyte) can be made to flow either in series, as in (1), or in parallel stream, as in (2).

*Types of Electrolytic Apparatus.*—There are numerous forms of apparatus for the preparation of electrolytic sodium hypochlorite. Kellner's, one of the first to be much used, may be taken as a type. The apparatus (Fig. 112) consists of a trough *A* of non-conducting material covered with a lid *B*, and provided on two opposite sides with grooved ribs *a*, *a*<sup>1</sup>, *a*<sup>2</sup>, . . . *a*<sup>*n*</sup> and *b*, *b*<sup>1</sup>, *b*<sup>2</sup>, . . . *b*<sup>*n*</sup>. These ribs are arranged so that those on one side face a space between two on the other, and vice-versa. Electrodes 1, 2, and 3, preferably of carbon, or metal plates covered on one side with platinum, are fitted into the grooves in the ribs, as shown in the figure, so that the free end of each projects into the space between the pair of ribs on the opposite side of

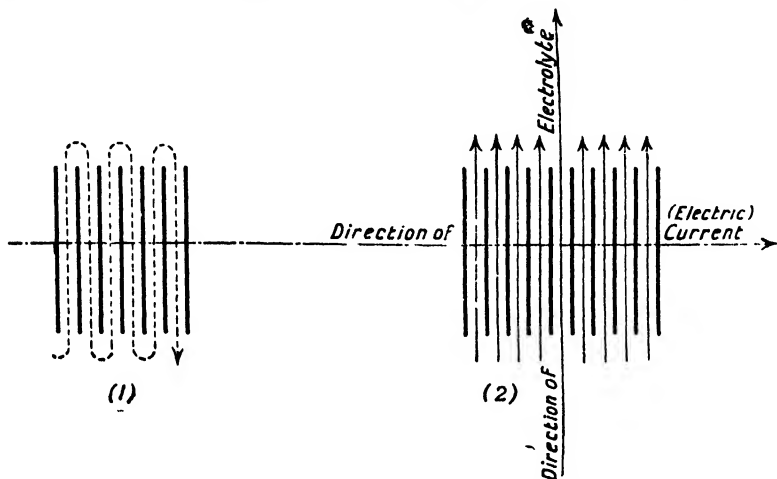
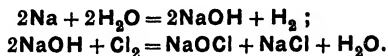


Fig. 111.—Directions of Current and Electrolyte.

the trough. The end electrodes project from the trough through the cover. The liquid to be electrolysed enters *A* through the pipe *D*, pursuing a zigzag course between the electrodes, and is discharged through *E*. The alternate arrangement of the electrodes converts each space between two neighbouring electrodes into a separate cell, one side of each electrode being an anode, and the other a cathode. Thus, supposing the current enters at the electrode 1, and leaves at the electrode *n*, the electrode 1 will then be an anode, the side of 2 next the electrode 1 being a cathode, and the further side acting as an anode, and so on. The arrangement is thus seen to be similar to a series of separate cells arranged in series, only two contacts being necessary, one for the first, and the other for the last electrode. The plan by which the free end of each electrode enters a space between two ribs prevents any portion of the current flowing from the fixed end of one electrode past the free end of the adjacent one, and through the electrolyte to the succeeding electrode. By this means loss of electrical energy is avoided, the current following the path of least resistance, and passing from electrode to electrode direct, without any portion taking the zigzag course followed by the electrolyte. The distance between the electrodes being very small, no diaphragms are used, so that the internal resistance of the apparatus can be made very small. As the solution of

common salt passes through the cells, chlorine is formed at all the anode sides of the electrodes, and caustic soda at the cathode sides. The rapid circulation of the liquid through the cells causes the chlorine formed to be at once brought into contact with the caustic soda, whilst the hydrogen formed at the cathodes is removed rapidly, and prevented from interacting with the sodium hypochlorite formed:



The bleaching liquid is conveyed through *E* back to the original reservoir, containing the material to be bleached, by means of a pump, so that constant circulation through the bleaching reservoir and decomposing apparatus is

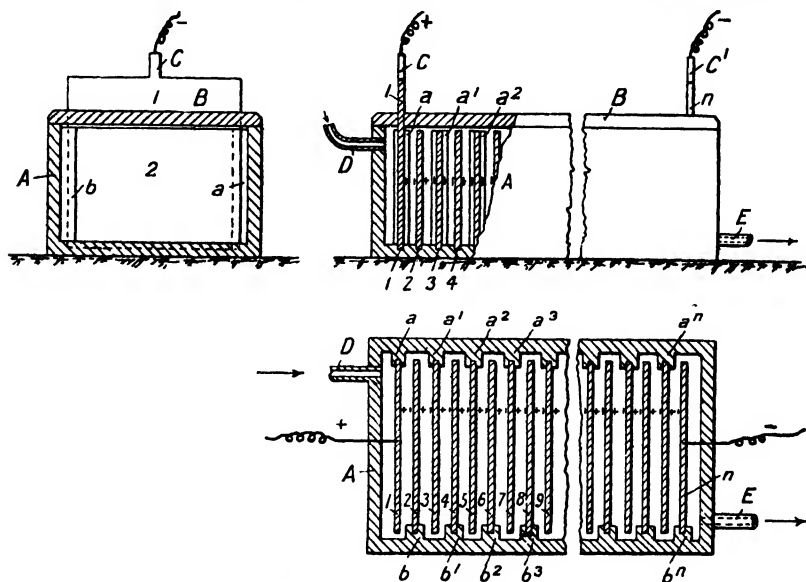
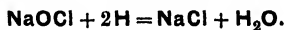


Fig. 112.—Kellner Electrolyser.

maintained. When carbon electrodes are employed, a filter is interposed between the decomposing tank and the bleaching reservoir; this filter may consist of glass-wool confined between perforated metal plates. Further information and other types of apparatus may be found in *The Principles of the Bleaching and Finishing of Cotton*, by Trotman and Thorp (Griffin & Co.).

There are some difficulties inseparable from any electrolytic process, due to the fact that water is decomposed at the same time as the salt solution, with the formation of hydrogen and oxygen. These cause secondary reactions to take place, such as the following:

(1) The hydrogen liberated at the cathode reduces some of the sodium hypochlorite to chloride:



(2) The oxygen oxidizes some of the hypochlorite to chlorate,  $\text{NaClO}_3$ .

Finally, a solution of sodium hypochlorite can be made by adding sodium carbonate to a clear solution of bleaching powder until no more precipitate is produced. If the exact strength of the bleaching powder solution is known,

and the quantity of calcium hydroxide it contains, the quantity of sodium carbonate necessary to precipitate the calcium as carbonate can be calculated, weighed out, and added. After the precipitated calcium carbonate has settled down, the clear solution contains sodium hypochlorite.

This method is rather clumsy. It is better to determine by direct experiment the exact quantity of sodium carbonate necessary for complete precipitation of the calcium.

Twenty-five millilitres of the clear or filtered bleaching powder solution is placed in a 250-ml. graduated flask. Sufficient normal acid is then added to produce a distinct acid reaction, and the mixture is boiled to expel the liberated chlorine. The liquid is then carefully treated with decinormal sodium hydroxide till it is exactly neutral to methyl orange. An excess (e.g. 50 ml.) of decinormal sodium carbonate solution is then added, and the mixture is again boiled for a few minutes. It is then cooled, made up to the mark with cold carbon-dioxide-free water, and mixed. After the precipitated calcium carbonate has settled, 50 ml. of the clear liquid is withdrawn by a pipette, and the excess of sodium carbonate present determined by titration with decinormal acid. From the quantity of sodium carbonate which has disappeared the amount required per gallon can be calculated.

*Example.*—Twenty-five millilitres of bleaching liquor was treated as described, and finally made up to 250 ml.

50 ml. of the clear liquor required	. 8.5 ml. of 0.1N. acid ;
∴ 250 ml. „ „ required	. 42.5 ml. „ „ ;

and  $50 - 42.5 = 7.5$  ml. of 0.1N. sodium carbonate required to precipitate 25 ml. of bleach liquor :

*i.e.*  $7.5 \times 0.0053$  or  $0.03975$  g. ;

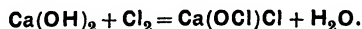
∴ 100,000 ml. require 159 g. ;

*i.e.* 1 gallon requires 111.3 grains.

If the sodium carbonate contains moisture, this must be allowed for. Thus for 95 per cent. sodium carbonate the quantity would be  $\frac{111.3}{95} \times 100$ .

A slight excess of sodium carbonate should be used if a stable solution is desired.

**Bleaching Powder, Chloride of Lime,  $\text{CaOCl}_2$ .**—This is the most important of the oxidizing bleaching agents, and is the one in commonest use for the vegetable fibres. It is prepared by exposing slaked lime to the action of chlorine gas :

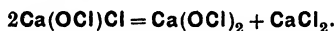


The slaked lime is spread on the floor of a specially constructed chamber, and the chlorine is led in through an opening at the top under a slight pressure. A glass window is provided, through which the progress of the absorption can be observed. As soon as the yellow colour of the chlorine disappears, more is introduced. This is repeated, the lime being also turned occasionally, until no more chlorine is absorbed, indicated by the permanent colour of the gas in the chamber. Some fresh slaked lime is then added to absorb the residual chlorine, and after this the powder is packed in air-tight drums. The temperature of the operation must be kept low, or calcium chlorate will be produced.

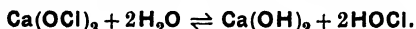
There is some doubt as to the constitution of bleaching powder. It is sometimes regarded as a molecular compound of calcium chloride and hypochlorite, having the formula  $\text{CaCl}_2 \cdot \text{Ca}(\text{OCl})_2$ . The chief evidence for this is that when dissolved in water the solution acts as though it contained both calcium chloride and hypochlorite. But dry bleaching powder cannot contain calcium chloride to any extent. Calcium chloride, like other deliquescent bodies, is soluble in alcohol. But an alcoholic extract of bleaching powder contains only traces of calcium chloride. Further, the available chlorine can be expelled by the action of carbon dioxide, which would not be the case if it were a double compound containing calcium chloride. When lime is completely saturated with chlorine gas, the maximum amount of chlorine which it absorbs is 43.5 per cent. This is in agreement with the formula  $\text{Ca}(\text{OCl})\text{Cl}$ . But in practice the chlorination of the lime is never complete, and 38 per cent. is the maximum of available chlorine present in commercial samples. Hence some unchanged slaked lime is always present, and ordinary bleaching powder is represented more nearly by the formula  $2\text{Ca}(\text{OCl})\text{Cl} + \text{Ca}(\text{OH})_2$ . But the quantity of free calcium hydroxide is very variable. It depends upon the care taken in manufacture.

**Properties.**—Bleaching powder is a white amorphous powder, which should contain no lumps. If pure lime has been used in its preparation, accompanied by complete chlorination, it is almost entirely soluble in water. If chlorination was incomplete, free calcium hydroxide will be present, which settles down as an insoluble *sludge* or precipitate when the powder is extracted with water. The use of a low-grade lime also increases the amount of insoluble matter present. Good commercial samples contain from 35 to 38 per cent. of chlorine which can be used for bleaching, or *available chlorine*, as it is generally termed.

Bleaching powder is hygroscopic, and deteriorates rapidly if exposed to air. When it takes up atmospheric moisture, or is treated with water, it undergoes molecular rearrangement, calcium chloride and hypochlorite being formed, both of which are soluble in water:



If free lime or calcium hydroxide is present, sufficient of this is dissolved to saturate the water, the remainder forming the sludge. The calcium hypochlorite also becomes hydrolysed to a certain extent by the water, with liberation of hypochlorous acid and calcium hydroxide:

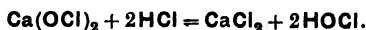


Finally, some free chlorine may be formed owing to the reversibility of the equation:

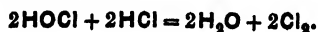


A solution of bleaching powder has thus a somewhat complex composition.

**Action of Acids.**—Strong acids such as hydrochloric and sulphuric acids liberate either hypochlorous acid or chlorine from a solution of bleaching powder according to the quantity used. When only small quantities are used, the chief product is hypochlorous acid:

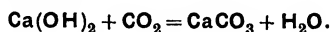


With more acid than is required by this equation the hypochlorous acid is decomposed, and chlorine is formed:

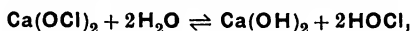


When weak acids such as boric acid are used, only hypochlorous acid is obtained with dilute solutions of bleaching powder. It has already been stated that this acid can be prepared by distilling a mixture of bleaching powder, water, and boric acid. Acids intermediate in strength (or hydrogen-ion concentration) between boric and the mineral acids give mixtures both of hypochlorous acid and chlorine. Organic acids and phosphoric acid act in this way.

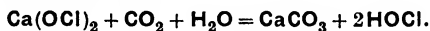
*The action of carbon dioxide* is peculiar and important. If a clear solution of bleaching powder is exposed to the air, it becomes turbid, owing to the formation of calcium carbonate by neutralization of the free calcium hydroxide by the carbon dioxide of the air:



The neutralization of this free lime affects the equilibrium of the equation:



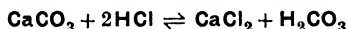
and more hypochlorous acid is produced till a new position of equilibrium is established. If more carbon dioxide is present than is required to combine with all of the calcium hydroxide, it decomposes the calcium hypochlorite, liberating more hypochlorous acid:



But some nascent chlorine is produced also. It has been stated above that the equation:



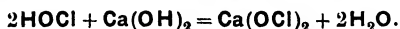
is reversible. Anything which either reduces the quantity of calcium hydroxide or increases the concentration of calcium chloride enables the reaction to proceed in the reverse direction, with the liberation of some chlorine. There may be also another explanation of the liberation of chlorine. Taylor found (*J. Soc. Chem. Ind.*, 1910, **29**, 1302) that the equation:



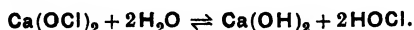
is reversible. That is, carbon dioxide can liberate small amounts of hydrochloric acid from calcium chloride. At the same time it reacts with calcium hypochlorite, producing hypochlorous acid, which in turn is decomposed by the hydrochloric acid produced by the first reaction. Thus a continuous cycle is established:

- (1)  $\text{CaCl}_2 + \text{H}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{HCl};$
- (2)  $\text{Ca(OCl)}_2 + \text{H}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{HOCl};$
- (3)  $\text{HCl} + \text{HOCl} = \text{H}_2\text{O} + \text{Cl}_2.$

*The action of alkalis* on bleaching powder solution is exactly the opposite to that of acids. Free hypochlorous acid is neutralized, and further hydrolysis is retarded or entirely inhibited. For example, with calcium hydroxide,



After neutralization of free hypochlorous acid, the effect of adding more calcium hydroxide is to increase the alkalinity of the solution which governs the reversible equation:

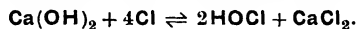


This tends to make the reaction proceed in the  $\leftarrow$  direction.

*Action of Salts on Bleaching Powder Solution.*—If calcium or sodium chloride is added to a solution of bleaching powder there is an immediate production of some nascent chlorine. The chlorine-like smell of the liquid is much more marked, and the colour of the solution becomes more like that of chlorine-water. There is some difference of opinion as to the reason for this action. Taylor (*J. Soc. Chem. Ind.*, 1910, **29**, 693, 1302) said that it is due to the reversibility of the equation:

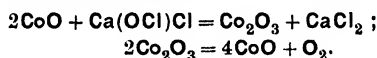


the addition of calcium or other soluble chloride causing reversion to take place. Higgins (*J. Soc. Chem. Ind.*, 1912, **31**, 486; 1913, **32**, 350) gives another explanation, namely, that it is due to the reversibility of the equation:



The bleaching powder solution contains calcium hydroxide, hypochlorite, chloride, and hypochlorous acid in a state of equilibrium, and the addition of some calcium chloride results in the formation of a new position of equilibrium at the expense of the generation of some chlorine.

*Action of Metals and their Oxides.*—Certain metals, including iron, copper, nickel, and cobalt, are attacked by cold solutions of bleaching powder, with formation of their oxides or hydroxides and evolution of oxygen. Other metals, such as aluminium and magnesium, liberate not oxygen but hydrogen. In the case of the metals which liberate oxygen, their oxides act in the same way. Moreover, they perform the function of a catalytic agent or oxygen-carrier. If a solution of bleaching powder is heated with only a small quantity of freshly precipitated cobaltous oxide,  $\text{CoO}$ , the whole of its oxygen will be liberated. The cobaltous oxide is first oxidized into cobaltic oxide by the bleaching powder. Cobaltic oxide then gives up part of its oxygen, reforming the original oxide, which again undergoes the same cycle of changes:



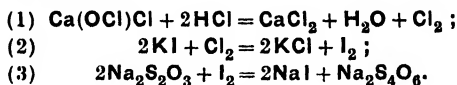
This action can be demonstrated also by adding some freshly prepared copper oxide to a concentrated bleaching powder solution and warming the mixture.

*Action of Sodium Thiosulphate.*—A solution of bleaching powder gives up its chlorine to sodium thiosulphate, forming sodium hydrogen sulphate and hydrochloric acid:



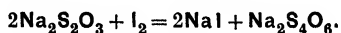
This reaction is of importance, since sodium thiosulphate is used in bleaching as an antichlor to free goods from chlorine.

*Analysis of Bleaching Powder.*—The value of a sample of bleaching powder is measured by the percentage of *available* chlorine which it contains, that is, capable of being liberated by excess of acid. The determination depends upon the reactions:



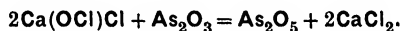
About 10 g. of the powder is weighed out, and mixed with water in a mortar till a thin cream is produced. After allowing the mixture to stand for

a few minutes, the liquid is decanted off into a litre flask, so as to leave the undissolved residue in the mortar. This is again ground with water and decanted, the process being repeated till the whole of the powder has been transferred to the flask. The solution is then made up to 1 litre with water, and thoroughly mixed. After shaking, and before the sediment has time to settle, 25 ml. is withdrawn with a pipette and placed in a beaker. About 1 g. of solid potassium iodide is then added, and a slight excess of acetic acid. This liberates the chlorine, which, in its turn, decomposes the potassium iodide, setting free its equivalent of iodine, as shown in the above equation. Decinormal sodium thiosulphate solution is now run in until most of the iodine has disappeared. A few drops of starch solution are then added and the addition of thiosulphate continued until the blue colour is just discharged. This will take place when the whole of the iodine has been converted into sodium iodide, in accordance with the equation:



Each millilitre of thiosulphate solution used corresponds to 0.00355 g. of chlorine, and hence the value of the bleaching powder can be calculated. Decinormal sodium thiosulphate solution is prepared by dissolving 24.8 g. of pure recrystallized thiosulphate in distilled water, and making the solution up to 1 litre. The starch solution may be made by pouring a cream, made by mixing 1 g. of soluble starch with water, into 100 ml. of boiling water.

Instead of sodium thiosulphate, a decinormal solution of arsenious acid may be employed. This body is oxidized by chlorine into arsenic acid, in accordance with the equation:



The arsenious acid is run in from a burette until a drop of the solution removed with a glass rod no longer turns iodized starch-paper blue. This paper is made by dissolving a little potassium iodide in starch solution, dipping a strip of filter-paper into the solution, and drying it. If a decinormal solution of arsenious acid be used, each millilitre used corresponds to 0.00355 g. of chlorine.

The arsenious acid solution is prepared in the following manner: Exactly 4.95 g. of pure arsenious acid is placed in a litre flask with 25 g. of crystalline sodium carbonate and about 200 ml. of distilled water. The mixture is boiled gently with shaking until solution is complete, after which it is cooled, and made up to a litre with water. The titration can be simplified by using indigo sulphate or indigo carmine as an indicator, this body being readily decolorized by chlorine. In this case, however, the operation is reversed. A measured quantity, say 25 ml., of the arsenious acid solution, together with a little hydrochloric acid, is placed in a flask, and a drop of indigo solution added. The bleach liquor is now run in from a burette with shaking till the colour is just discharged or a yellowish tint obtained.

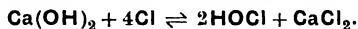
Bleaching powder is rarely adulterated, although it may often be below the mark as regards available chlorine. If the temperature has been too high in the course of manufacture, it may contain traces of chlorates. These are very objectionable, since they cause over-bleaching when used on cotton. Iron oxide is sometimes present in distinct quantities in bleaching powder. The danger attached to its presence has already been mentioned. The examples of commercial bleaching powder given in Table XL are taken from Thorpe's *Dictionary of Applied Chemistry*.



**Action of Salts on Bleaching Powder Solution.**—If calcium or sodium chloride is added to a solution of bleaching powder there is an immediate production of some nascent chlorine. The chlorine-like smell of the liquid is much more marked, and the colour of the solution becomes more like that of chlorine-water. There is some difference of opinion as to the reason for this action. Taylor (*J. Soc. Chem. Ind.*, 1910, **29**, 693, 1302) said that it is due to the reversibility of the equation:

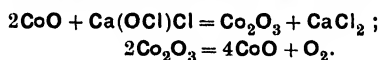


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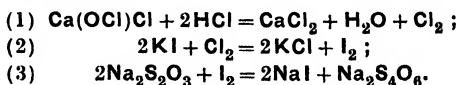
This action can be demonstrated also by adding some freshly prepared copper oxide to a concentrated bleaching powder solution and warming the mixture.

**Action of Sodium Thiosulphate.**—A solution of bleaching powder gives up its chlorine to sodium thiosulphate, forming sodium hydrogen sulphate and hydrochloric acid:



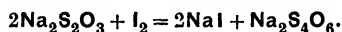
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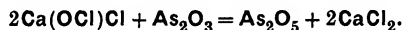
About 10 g. of the powder is weighed out, and mixed with water in a mortar till a thin cream is produced. After allowing the mixture to stand for

a few minutes, the liquid is decanted off into a litre flask, so as to leave the undissolved residue in the mortar. This is again ground with water and decanted, the process being repeated till the whole of the powder has been transferred to the flask. The solution is then made up to 1 litre with water, and thoroughly mixed. After shaking, and before the sediment has time to settle, 25 ml. is withdrawn with a pipette and placed in a beaker. About 1 g. of solid potassium iodide is then added, and a slight excess of acetic acid. This liberates the chlorine, which, in its turn, decomposes the potassium iodide, setting free its equivalent of iodine, as shown in the above equation. Decinormal sodium thiosulphate solution is now run in until most of the iodine has disappeared. A few drops of starch solution are then added and the addition of thiosulphate continued until the blue colour is just discharged. This will take place when the whole of the iodine has been converted into sodium iodide, in accordance with the equation:



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Bleaching powder is rarely adulterated, although it may often be below the mark as regards available chlorine. If the temperature has been too high in the course of manufacture, it may contain traces of chlorates. These are very objectionable, since they cause over-bleaching when used on cotton. Iron oxide is sometimes present in distinct quantities in bleaching powder. The danger attached to its presence has already been mentioned. The examples of commercial bleaching powder given in Table XL are taken from Thorpe's *Dictionary of Applied Chemistry*.

TABLE XL.—COMPOSITION OF SAMPLES OF BLEACHING POWDER.

	A, per cent.	B, per cent.	C, per cent.
Available chlorine . . .	37.00	38.30	36.00
Chlorine as chloride . . .	0.35	0.59	0.32
Chlorine as chlorate . . .	0.25	0.08	0.26
Lime . . . . .	44.49	43.34	44.66
Magnesia . . . . .	0.40	0.31	0.43
Ferric oxide . . . . .	0.05	0.04	0.02
Alumina . . . . .	0.43	0.41	0.33
Oxide of manganese . . .	Trace	Trace	Trace
Carbon dioxide . . . . .	0.18	0.30	0.48
Siliceous matter . . . . .	0.40	0.30	0.50
Water and loss . . . . .	16.45	16.33	17.00

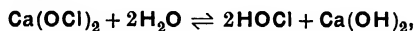
A sample of bleaching powder made from pure lime under the best conditions gave:

Available chlorine . . . . .	43.13 per cent.
Chlorine as chloride . . . . .	0.29 " "
Lime . . . . .	39.89 " "
Carbon dioxide . . . . .	0.42 " "
Water . . . . .	17.00 " "

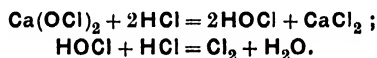
**Use of Bleaching Powder in Bleaching.**—Animal fibres cannot be bleached by means of chlorine or bleaching powder. Proteins or amino compounds, such as wool and silk, are rapidly converted into chloramines, and if excess of bleaching powder or chlorine is present the fabrics are completely disintegrated or dissolved. Vegetable fibres, such as cotton, are nearly always bleached by means of a solution of bleaching powder, and if the operation is carried out under suitable conditions the fibre is not damaged. But unsuitable conditions, such as excess of the bleaching agent, too high a temperature, or the presence of catalytic agents such as metallic oxides, cause the cellulose of the cotton to become partly or entirely changed into oxycellulose. A clear solution of the powder is used, obtained by stirring it with water and allowing the sludge to settle. Such a solution has, however, comparatively little bleaching action. The bleaching action becomes marked only under conditions which ensure that either nascent chlorine or free hypochlorous acid or both are present. From the description of the properties of bleaching powder given above, it will be seen that these bodies could be produced by the addition of a strong acid, such as sulphuric or hydrochloric. But it would be very difficult with these acids to get anything but chlorine, which would probably cause *over-bleaching*, i.e. the production of oxycellulose. With a weak acid there is less chlorine and more hypochlorous acid, the ratio of these depending upon the hydrogen-ion concentration of the acid used. Both the cheapest and best acid to employ is the carbon dioxide of the atmosphere. This is always done in bleaching, and the bleacher obtains it by aeration of either the goods or the bleaching liquor. The reactions which take place are complicated, and, as explained above, the subject of some discussion. But the action may be explained in the following way:

(1) When the bleaching powder is treated with water, a solution of calcium

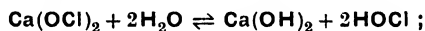
hypochlorite and calcium chloride is obtained, together with some calcium hydroxide. (2) The calcium hypochlorite becomes hydrolysed into hypochlorous acid and calcium hydroxide, till the concentration of the latter establishes a position of equilibrium. (3) At the same time some nascent chlorine is produced. (4) Both the hypochlorous acid and the nascent chlorine bleach the colouring matter of the cotton, but more of them is required than can be present by this mechanism. (5) Atmospheric carbon dioxide, however, neutralizes some of the calcium hydroxide in the solution. This destroys the equilibrium of the equation:



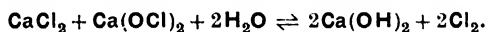
and causes more hypochlorous acid to be liberated by hydrolysis, or, if Taylor's views are accepted, the liberation of chlorine. This process continues as long as carbon dioxide is present. Thus, bleaching powder owes its bleaching effect to the action of atmospheric carbon dioxide. Without this, its action is insignificant. The action of carbon dioxide is slow and regular, air containing not more than 0.05 per cent. If it is necessary to hasten the action, small quantities of another acid may be added, but this is dangerous, since it is difficult to add just the right amount, and not so much as to cause a rapid evolution of chlorine:



Temporary stimulation of bleaching action may be brought about by adding some calcium chloride to the solution. There are two ways of explaining this action (see above). If it is desired to retard the rate of bleaching, this can be done by the cautious addition of a little alkali, such as lime-water. This acts by inhibiting the hydrolysis of the calcium hypochlorite:



and also tends to reverse the reaction:



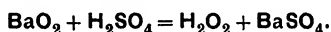
## CHAPTER XVIII.

### NON-CHLORINATED OXIDIZING BLEACHING AGENTS.

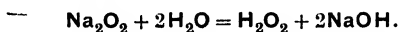
**Hydrogen peroxide**,  $\text{H}_2\text{O}_2$ , is a bleaching agent of great value, especially for wool and silk, which are decomposed by chlorine. It is made by treating certain metallic peroxides or higher oxides with a dilute acid. These metallic compounds are of two kinds: (i) those which give hydrogen peroxide with acids, and (ii) those which give oxygen. The peroxides of the alkali and alkaline-earth metals belong to the first class, while the second includes such oxides as manganese dioxide, which with sulphuric acid gives



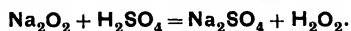
Hydrogen peroxide may be made from barium peroxide, by making it into a cream with water, and stirring this into cold dilute sulphuric acid in the proportion required by the equation:



After the insoluble barium sulphate has settled down, the clear liquid is drawn off. Any excess of sulphuric acid may be removed by the careful addition of barium carbonate. Phosphoric acid or hydrofluoric acid may be used in place of sulphuric acid, since both give insoluble barium salts. Hydrogen peroxide, together with sodium hydroxide, is obtained also when sodium peroxide is dissolved in water:



A neutral or faintly acid solution is made by stirring the powdered peroxide into the requisite quantity of dilute sulphuric acid:



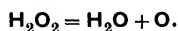
The soluble sodium sulphate remains in the solution.

*Commercial hydrogen peroxide* is an aqueous solution containing a little free acid or other stabilizing body. Both neutral and alkaline solutions are comparatively unstable, and deteriorate on keeping. Various bodies, such as phosphoric acid, dilute mineral acids, glycerol, or naphthalene, retard the rate of natural decomposition. Hydrogen peroxide is sold generally in two forms, known as *ten- to twelve-volume peroxide* and *one-hundred-volume peroxide*. This refers to the volume of oxygen gas which can be obtained from the solution. Ten-volume peroxide gives ten times its volume of oxygen, corresponding to 3 per cent. by weight of peroxide,  $\text{H}_2\text{O}_2$ . One-hundred-volume peroxide, also called *perhydrol*, contains 30 per cent. of hydrogen peroxide by weight, and yields one-hundred times its volume of oxygen. It is much more economical in use than the ten-volume peroxide. These concentrated forms are made in the following way: Sodium peroxide is stirred into a

20 per cent. solution of sulphuric acid at a low temperature. The sodium sulphate produced is more than sufficient to saturate the solution, and part of it crystallizes out as  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . Owing to the water of crystallization further concentration of the solution also is brought about. After removing the crystals of sodium sulphate, the solution is concentrated in a vacuum at a low temperature, and then frozen.

**Properties of Hydrogen Peroxide.**—Pure  $\text{H}_2\text{O}_2$  may be obtained from its concentrated solutions, made as described above, by fractionally distilling under reduced pressure and freezing the distillates. It is said to be a viscous, colourless liquid, which blisters the skin. It has a faintly acid reaction and a bitter taste. Its specific gravity is 1.5, and it is soluble in water in all proportions.

Pure hydrogen peroxide is comparatively stable in the absence of catalysts. It boils at  $84^\circ$  to  $85^\circ$  C. at a pressure of 68 millimetres. When heated at ordinary pressure it decomposes rapidly, with the evolution of oxygen gas. This decomposition begins at about  $50^\circ$  C., and is represented by the equation:



The bleaching action of hydrogen peroxide is due entirely to this liberated oxygen, and this decomposition takes place more readily in the presence of colouring matters. It is retarded, as noted above, by acids, but hastened by the presence of alkalis. Hydrogen peroxide cannot, therefore, be stored in glass bottles, unless sufficient acid is also present to neutralize any alkali dissolved. Glass containers for hydrogen peroxide are frequently coated internally with paraffin wax.

Metals, metallic oxides, and particles of dirt are still more active in bringing about the decomposition of hydrogen peroxide, acting as catalytic agents. Containers, or bleaching vessels, must never be made of metal. They consist generally of slate or wood.

Weber (*J. Soc. Dyers Col.*, 1923, **39**, 209) says that iron, manganese, and copper, or their salts, are particularly active as catalysts. He estimated the loss of oxygen in a one-volume solution of hydrogen peroxide at  $100^\circ$  F. ( $37.8^\circ$  C.) in the presence of small quantities of salts of iron and copper. In the case of the iron salt the bath lost all its oxygen in three hours, while in the presence of a copper salt two-thirds was lost in the same time. Tin, nickel, and lead have less action, lead being the least active of all.

Metallic catalysts are also the cause of little holes in bleached goods, or tenderness which subsequently develops into bad wearing power. This is seen from the following experiment: Skeins of Botany yarn were spotted with solutions of metallic salts containing 0.05 per cent. of the metal. They were then dried, and bleached at pH 10, using sodium silicate to neutralize the bath. The tensile strengths of the bleached yarn were:

Control skein	.	.	.	.	.	7.0 lbs.
Spotted with copper	.	.	.	.	.	2.1 "
" " iron	.	.	.	.	.	2.3 "
" " manganese	.	.	.	.	.	6.3 "

When hydrogen peroxide is used as a bleaching agent, a certain amount of instability is necessary, and a certain quantity of a mild alkali, such as ammonia, sodium silicate, or sodium phosphate, is added to the bath. But while a bleaching bath must be faintly alkaline, it must not contain sufficient alkali to make it so unstable that the oxygen escapes without exercising any bleaching action.

permanganate is run in from a burette till a permanent faint pink colour is produced. The reaction is



If the first drop of permanganate causes a pink colour, more sulphuric acid must be added—that is, a considerable excess is required. The hydrogen peroxide may be expressed either as a percentage or as the volume of oxygen liberated. If the percentage is required, then each millilitre of decinormal permanganate is equivalent to 0.00170 g. of hydrogen peroxide. Since 3.036 g. of hydrogen peroxide evolves 1000 ml. of oxygen at 0° C. and 760 mm. pressure, 0.0017 g. will give 0.5603 ml. If a permanganate solution containing 5.641 g. per litre is used, each millilitre is equivalent to 1 ml. of oxygen at 0° C. and 760 mm. pressure.

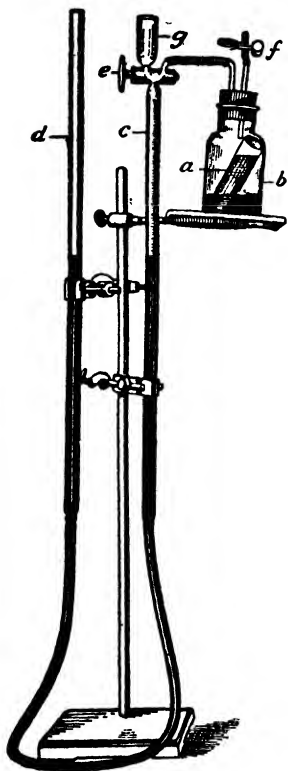
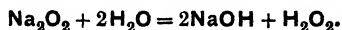


Fig. 113.—Apparatus for estimating Hydrogen Peroxide.

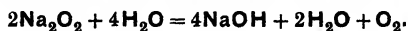
The volume of oxygen produced may be measured directly by the following method: A nitrometer *c* (Fig. 113) is completely filled with water, and connected with the bottle *b* as shown. The bottle contains a solution of potassium permanganate and dilute sulphuric acid. In *a* is placed a measured volume (e.g. 1 ml.) of the peroxide. By raising the reservoir *d* and opening the three-way tap *e* to the air, the graduated tube *c* is completely filled to the tap with water. The tap is then closed, and the pinchcock *f* is opened for a moment to bring the air in the bottle to atmospheric pressure. The reservoir *d* is then lowered, and the tap is turned so that the nitrometer is connected to the bottle. The peroxide is then mixed with the acid permanganate by carefully tilting the bottle. Oxygen gas is given off. After allowing it to cool, the reservoir *d* is raised till the level of the water is the same in both tubes. The volume of air displaced from the bottle by the oxygen is then read off.

**Sodium peroxide**,  $\text{Na}_2\text{O}_2$ , is prepared by passing dry air, free from carbon dioxide, over shavings of metallic sodium heated to a temperature of 400° C.

It forms a yellowish powder containing from 95 to 98 per cent. of peroxide. A crystalline hydrate,  $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ , has also been prepared. Sodium peroxide is soluble in water, but is also decomposed by it. When it is dissolved in cold water, hydrogen peroxide and sodium hydroxide are formed, as shown by the equation:



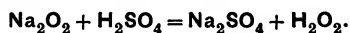
If, however, the solution is heated, or warm water is used to dissolve the peroxide, sodium hydroxide and oxygen are obtained:



Sodium peroxide may be used in this way for the preparation of either hydrogen peroxide or oxygen. To obtain the latter, fused sticks or balls of the peroxide are more convenient than the powder. Although stable in dry

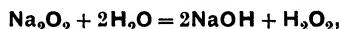
air, sodium peroxide deteriorates rapidly if exposed to a damp atmosphere, and loses its oxygen. It must be kept in closed air-tight vessels. When it dissolves in water, considerable heat is evolved. If water is poured on to dry peroxide, the temperature is quickly raised to that necessary for the second reaction, given above, and only oxygen is obtained. This may be given off so rapidly as to cause an explosion. To prepare a solution containing hydrogen peroxide, the powder must be stirred slowly into an excess of cold water. On account of the readiness with which sodium peroxide gives off oxygen, it is a very powerful oxidizing agent. If wool is mixed with the powder and gently warmed, or the mixture touched with a hot copper wire, the oxidation is so energetic that the wool bursts into flame. Fires can be caused by leaving sodium peroxide lying about in contact with organic matter. If a little methylated spirit is poured on to dry sodium peroxide, it burns without the application of heat.

A solution of sodium peroxide in cold water has naturally all the properties of one containing hydrogen peroxide. But such a solution could not be used for bleaching on account of the presence of sodium hydroxide. This must first be neutralized with an acid. Since sodium peroxide is itself decomposed by acids with the production of hydrogen peroxide and the sodium salt of the acid used, this method is generally used in preparing bleaching solutions, *i.e.* the peroxide is stirred into a slight excess of dilute sulphuric acid. The reaction is



Such solutions, after being rendered faintly alkaline, are used for bleaching in exactly the same way as hydrogen peroxide.

From the equation:

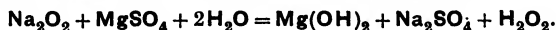


it is seen that 78 parts of sodium peroxide produce 34 of hydrogen peroxide.

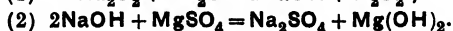
Hence, 3 parts of hydrogen peroxide are obtained by dissolving  $\frac{78 \times 3}{34}$ , *i.e.* 6.88, parts of sodium peroxide in water. Now, ten-volume hydrogen peroxide contains 3 per cent. by weight of peroxide. Hence, if 6.88 lb. of sodium peroxide is dissolved in 10 gallons (*i.e.* 100 lb.) of water or dilute sulphuric acid, a ten-volume solution of hydrogen peroxide is obtained.

Commercial sodium peroxide is a very pure substance containing generally not less than 98 per cent. of  $\text{Na}_2\text{O}_2$ . Assuming the sample to be of 98 per cent. strength, the quantity would be  $\frac{6.88 \times 100}{98}$ , *i.e.* 7.02 lb.

Another method of treating sodium peroxide is to dissolve it in water containing more magnesium sulphate than is required by the equation:



In this way a turbid bath containing insoluble magnesium hydroxide is obtained, which will contain the comparatively stable magnesium hydroperoxide,  $\text{Mg}(\text{HO}_2)_2$ , mentioned above. The reaction given above actually takes place in two stages, *viz.*:



Magnesium sulphate is often used in this way to replace a strong caustic alkali by a weak one. If crystalline magnesium sulphate or Epsom salts,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , is used, 246.5 parts are required for each 78 parts of sodium

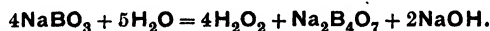


peroxide. An advantage connected with the use of sodium peroxide for bleaching is the economy accruing from its much greater compactness. It is undoubtedly cheaper to use than commercial hydrogen peroxide, but, of course, it must be kept in air-tight receptacles. Water used in making up solutions must be perfectly free from iron. If this is present, iron oxide is formed, which, as with ordinary hydrogen peroxide, causes rapid decomposition of the solution. For the same reason iron-free sulphuric acid must be employed. Hydrochloric acid is safer to use than sulphuric, since it is more easily obtained free from iron. It has also another advantage, namely, that when diluted with water it does not produce nearly so much heat as sulphuric acid.

*Analysis of Sodium Peroxide.*—A weighed quantity, from 1 to 2 g., of the peroxide is stirred into dilute sulphuric acid, and the solution made up to a definite volume, say 500 ml. The hydrogen peroxide is then titrated with decinormal potassium permanganate.

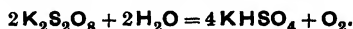
**Perborates** are salts of perboric acid,  $\text{HBO}_3$ , which does not exist in the free state. Sodium perborate is obtained when solutions of borax are treated at a low temperature with hydrogen peroxide, or vice-versa, boric acid with sodium peroxide.

The formula of sodium perborate is not certain, but it may be  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ . The perborates are white compounds, which are not very soluble in water. In aqueous solution they decompose gradually into a mixture of borax, hydrogen peroxide, and sodium hydroxide:

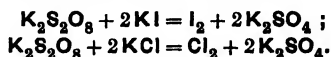


They are valuable bleaching agents on account of their limited solubility and the slowness with which they are decomposed, but are too expensive for general use. Solutions of perborates are affected by catalysts in the same way as those of hydrogen peroxide.

**Persulphates** have some value as bleaching agents. The most important are the potassium and ammonium salts, which are made by electrolysis of a solution of dilute sulphuric acid saturated with potassium or ammonium sulphate. The persulphates are salts of an acid of the composition  $\text{H}_2\text{S}_2\text{O}_8$ , though another form,  $\text{H}_2\text{SO}_5$ , is also known. They are powerful oxidizing agents, owing to the liberation of nascent oxygen by the action of water:

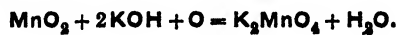


This liberation of oxygen is very slow at temperatures up to  $30^\circ\text{C}$ . Above this, the rate increases gradually with rise in temperature. Their action can, therefore, be controlled readily. Catalysts, such as salts of iron or copper, accelerate the rate of decomposition. Another important property of persulphates is their power of liberating the halogen elements from their compounds. When sodium chloride or iodide is added to a solution of a persulphate, chlorine or iodine is gradually liberated:

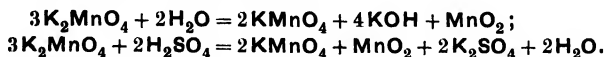


Persulphates may thus be made to give rise to oxygen or chlorine as desired.

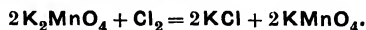
**Potassium permanganate**,  $\text{KMnO}_4$ , is a derivative of manganese heptoxide,  $\text{Mn}_2\text{O}_7$ . When manganese dioxide,  $\text{MnO}_2$ , is fused with potassium hydroxide in the presence of air or an oxidizing agent, such as potassium nitrate, potassium manganate is formed:



The fused mass has a green colour, and, in the presence of the excess of alkali, dissolves in water, giving a green solution of the manganate. If this solution is acidified or largely diluted, it is decomposed, and potassium permanganate is formed as one product of the reaction:



The presence of permanganate is indicated by the formation of a purple-coloured solution. The same change is brought about by the action of chlorine on the solution of potassium manganate:

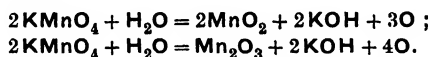


Potassium permanganate is a purple, crystalline substance, which dissolves in water, giving a deep purple-coloured solution. Though stable by itself, either as a solid or in solution, yet in the presence of an oxidizable body it becomes unstable, and has a powerful oxidizing action, giving up a part of its oxygen, which being in the nascent state is very active. If potassium permanganate is represented by the formula  $\text{Mn}_2\text{O}_7 \cdot \text{K}_2\text{O}$  (i.e.  $2\text{KMnO}_4$ ), its oxidizing action is due to its reduction to manganous oxide,  $\text{MnO}$ :

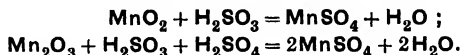


Thus  $2\text{KMnO}_4$  contains five atoms of oxygen available for oxidation or bleaching. But the whole of this oxygen cannot be made use of unless an acid is used as well.

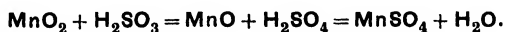
If cotton is soaked in a solution of potassium permanganate in water, it becomes coated with a brown deposit consisting of a mixture of manganese dioxide and sesquioxide:



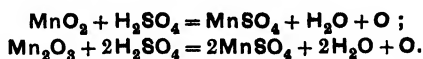
These reactions are made use of in dyeing with manganese brown or bistre. The oxygen which is produced at the same time bleaches the cotton, but the effect is obscured by the presence of the brown oxides. These can be dissolved by means of sulphurous acid, when the bleaching becomes apparent:



Manganese dioxide and sesquioxide will not dissolve in cold sulphuric acid, but the sulphurous acid reduces them to manganous oxide,  $\text{MnO}$ , which is soluble, thus:



Two points should be noted in connection with the above reactions: firstly, when an aqueous solution of permanganate is used, free caustic alkali is produced; and secondly, part of the oxygen is wasted as a bleaching agent. The free caustic alkali would always be objectionable in bleaching textile fabrics; the loss of oxygen would tend to make the process unnecessarily expensive. The alkali can be neutralized as it is produced by adding sulphuric acid to the bath. Moreover, if sufficient sulphuric acid is used, the manganese dioxide and sesquioxide are decomposed, with the liberation of their loosely combined oxygen:

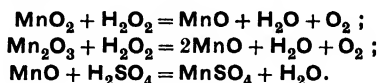


In this way not only can the liberation of alkali be prevented, but also the whole of the oxygen is made use of. The reaction would be

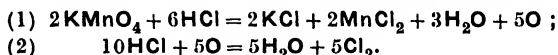


In practice, however, much more acid is required than the proportions given by the equation, but if the solution contains about 5 per cent. of sulphuric acid no deposition of the oxides of manganese takes place.

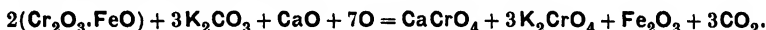
There is another way in which the precipitated oxides may be treated. When brought into contact with a dilute acidified solution of hydrogen peroxide they are decomposed, with the liberation of oxygen, which is available for bleaching. Manganous oxide,  $\text{MnO}$ , is produced at the same time, and dissolves in the acid present:



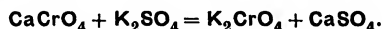
Hydrochloric acid must not be used with permanganate, since chlorine is produced:



**Potassium dichromate**,  $\text{K}_2\text{Cr}_2\text{O}_7$ , also is a very powerful oxidizing agent. It is not used for bleaching, though it has many other important textile uses. It is made from chrome iron ore, which is first converted into a mixture of calcium and potassium chromates by roasting it with potassium carbonate and lime in a reverberatory furnace:



The roasted mass is cooled, broken up, and treated with a hot solution of potassium sulphate. This decomposes the calcium chromate, forming potassium chromate and sparingly soluble calcium sulphate:



The calcium sulphate settles down as a precipitate, and the clear liquor containing the dissolved potassium chromate is then treated with sulphuric acid, which changes the chromate into dichromate and potassium sulphate:

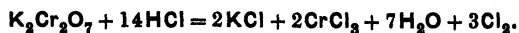


The potassium dichromate is much less soluble in water than potassium sulphate, and can be separated from it by crystallization. The residual liquor containing the potassium sulphate is used over again, and the crude potassium dichromate purified by recrystallization.

Potassium dichromate is a reddish crystalline substance, which is not very soluble in water, giving a solution with an acid reaction. It is supposed to be a salt of dichromic acid,  $\text{H}_2\text{Cr}_2\text{O}_7$ , though the acid is not known in the free state. It contains three atoms of loosely combined oxygen, but gives them up only in the presence of an acid, such as sulphuric:

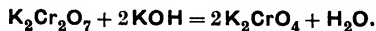


With hydrochloric acid the oxygen is not liberated, since it oxidizes the acid to chlorine:



A mixture of potassium dichromate and sulphuric acid is used for stripping dyestuffs, oxidizing aniline to aniline black, mordanting wool, and for other purposes.

When a soluble dichromate is treated with an alkali, it is converted into the corresponding chromate:



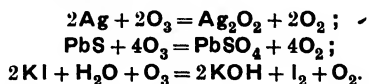
It has been noted above that, vice-versa, a chromate is changed into a dichromate by acids. These reactions are of importance in dyeing with the metachrome dyes.

**Sodium dichromate**,  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , is much more soluble in water than the potassium salt: 100 parts of water at  $0^\circ \text{C}$ . dissolve 5 of potassium and 62 of sodium dichromate.

**Air as a Bleaching Agent.**—In the bleaching of linen, exposure to the action of air, or *grassing*, is employed to improve the colour or partly bleach the goods. Air alone has very little bleaching action. The presence of the ultra-violet rays in diffuse daylight is essential. It is thought, also, that the presence of traces of ozone and hydrogen peroxide plays an important part in the action. The process is a very slow one, and it is practicable only in country districts where the air is free from particles of floating soot or dirt. Attempts have been made to shorten the process. For example, Müller (*J. Soc. Chem. Ind.*, 1910, 29, 1200; 1911, 30, 534) proposed to bleach cotton by boiling it with an alkaline solution, such as sodium hydroxide or milk of lime, and passing a stream of air through the boiling liquor. A little manganese salt is added to the alkaline lye to act as an oxygen-carrier. Such a method could obviously be applied only to a vegetable fibre which is not damaged by boiling alkalis. In the case of cotton, the production of oxycellulose would be likely to spoil the process.

**Ozone**,  $\text{O}_3$ , is an allotropic form of oxygen, which has very powerful oxidizing and bleaching properties. It is obtained, mixed with air, when the latter is subjected to the action of a silent electric discharge. The slow oxidation of phosphorus and other bodies also gives rise to ozone. Apparatus for the production of large quantities of ozonized air is made by the Ozonair Company. Fig. 114 illustrates one of these. The air is filtered and dried, and after cooling passes through the ozonizer, which is connected with a main electric supply. If this is alternating, it can be used directly, but if not, the current passes through a transformer. An apparatus of this type is capable of producing 120 litres of ozonized air per minute.

Ozone has a very characteristic smell, and is a powerful oxidizing agent. It is absorbed by turpentine and some other unsaturated organic compounds. Its oxidizing power is illustrated by the following, among other examples: it oxidizes metallic silver to silver peroxide, lead sulphide to lead sulphate, and liberates iodine from potassium iodide:



In all of these and similar cases oxygen is produced.

The presence of ozone in air may be detected by means of its reaction with potassium iodide: if a piece of filter-paper is moistened with a mixture of starch-paste and potassium iodide, and exposed to the action of ozonized air, it immediately turns blue owing to the formation of iodide of starch. Of course, everything which does this is not ozone; hydrogen peroxide will do the same,

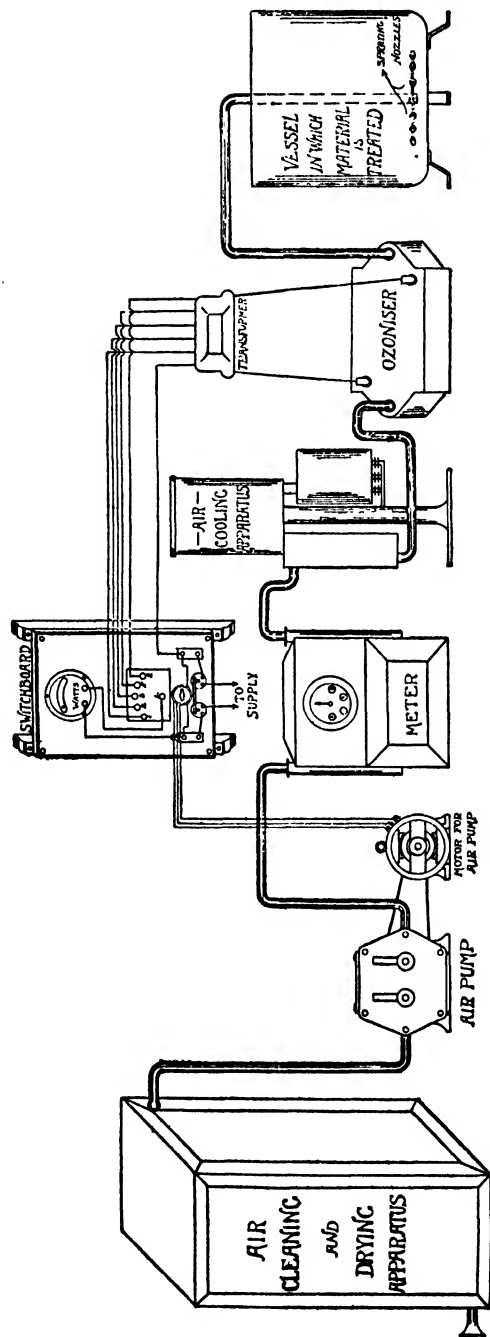


Fig. 114.—Ozone Plant.

but no other oxidizing agent will oxidize clean metallic silver to silver oxide. When ozone is brought into contact with platinum black, lead dioxide, or manganese dioxide, it is converted into oxygen, the platinum black or metallic oxide acting as a catalyst.

It is claimed by the Ozonair Company that ozonized air of a concentration not exceeding 0.5 g. of ozone per cubic metre may be used for bleaching wool. It has not been used for cotton, though it is said to be able to replace the grassing process in linen-bleaching. But owing to its great oxidizing power it must be used carefully. Air containing much ozone gradually destroys wool, and changes cotton into oxycellulose.

## CHAPTER XIX.

### ORGANIC SOLVENTS.

THE use of organic solvents for the removal of oil and grease from textile fabrics is increasing rapidly. They are used not only by themselves as a substitute for scouring with soap and water, but also in conjunction with soap, and in the preparation of liquids which are employed for the removal of local grease patches, as levelling agents in the dye-bath, or as capillarizing solutions. There are several different types of organic solvents suitable for these purposes. The commoner are—

- (1) Petroleum fractions of a comparatively low boiling-point, consisting chiefly of mixtures of aliphatic hydrocarbons of the general formula  $C_nH_{2n+2}$ .
- (2) Benzene or coal-tar hydrocarbons, consisting chiefly of benzene,  $C_6H_6$ .
- (3) Chlorinated hydrocarbons of either aliphatic or aromatic origin.
- (4) Hydrogenated aromatic hydrocarbons or their derivatives.

Some of these will be described briefly.

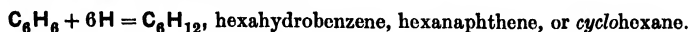
**Petroleum spirit** is found in various parts of the earth, and is obtained by boring wells into the oil-bearing strata. It is thought to have been produced either by dry distillation of coal beds by the natural heat of the earth or from the decomposition of the fatty constituents of prehistoric animals. In the crude state it is a thick brownish oil. Different kinds of oil differ in composition, and, hence, in the products obtained when they are distilled. American oil gives chiefly mixtures of paraffins—that is, hydrocarbons of the methane series, represented by the general formula  $C_nH_{2n+2}$ . The crude oil is distilled, and the fractions coming over between boiling-points are collected separately. These are (Kipping and Kipping, *Organic Chemistry*, p. 64)—

	Boiling-point.
(i) Petroleum ether . . . . .	40° to 70° C.
(ii) Gasoline . . . . .	70° to 90° C.
(iii) Light petroleum . . . . .	80° to 120° C.
(iv) Petrol and cleaning oil . . . . .	120° to 150° C.
(v) Kerosene, or burning oil . . . . .	150° to 300° C.
(vi) Lubricating oils . . . . .	Above 300° C.

The fraction boiling between 80° and 120° C. is known also as *solvent naphtha*, or sometimes as *benzine*. This is the portion used as a solvent in textile operations. It contains a large proportion of heptane,  $C_7H_{16}$ .

Caucasian petroleum, obtained chiefly from Baku, contains much less of the volatile constituents than American petroleum. It boils at about 150° C., and contains approximately 10 per cent. of benzene,  $C_6H_6$ , and higher members of the same series up to cymene,  $C_{10}H_{14}$ . It contains also a much smaller proportion of the paraffin hydrocarbons, but, instead, others of the general

formula  $C_nH_{2n}$ , termed *naphthenes*, such as octanaphthene,  $C_8H_{16}$ , and nononaphthene,  $C_9H_{18}$ . These are identical with the hydrogenated benzene hydrocarbons of the same formula, thus:



A somewhat similar spirit is produced, also, by the distillation of petroliferous shale.

All of these solvents are colourless, inflammable liquids with a specific gravity ranging from 0.65 to 0.75. Their inflammability depends upon the proportion of hydrocarbons present with low boiling-points. They are all insoluble in and immiscible with water.

**Benzene (benzole),  $C_6H_6$ ,** is obtained by the distillation of coal-tar. It boils at  $80.5^\circ C.$ , and burns with a luminous flame. Commercial benzene contains generally small quantities of other hydrocarbons of the same series, such as toluene,  $C_7H_8$ . It is a more powerful solvent than petroleum. Thus, some of the cotton waxes are insoluble in petrol, but dissolve readily in boiling benzole. It dissolves also sulphur and resins, which petrol is unable to do.

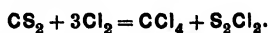
Solvents of the above classes have often a rather extended range of boiling-points, particularly those derived from American petroleum. Table XLI illustrates the differences met with in commercial samples. As a general rule, it is advantageous to have as short a range of boiling-points as possible. Perhaps the best results would be obtained with a solvent having a constant boiling-point of about  $110^\circ C.$  When the mean boiling-point is above  $100^\circ C.$  goods may be degreased without previous drying, but fractions with very high boiling-points are more difficult to recover from the degreased goods.

TABLE XLI.—FRACTIONATION OF COMMERCIAL PETROLEUM SOLVENTS.

Boiling-point of Fraction.	1.	2.	3.	4.
Up to $70^\circ C.$ . . . . .	2.5	1.0	0.0	2.0
From $70^\circ$ to $80^\circ C.$ . . . . .	21.5	2.0	25.0	4.0
From $80^\circ$ to $90^\circ C.$ . . . . .	31.0	12.0	33.0	14.0
From $90^\circ$ to $100^\circ C.$ . . . . .	24.0	82.0	16.0	33.0
From $100^\circ$ to $110^\circ C.$ . . . . .	13.0	3.0	14.0	26.5
Above $110^\circ C.$ . . . . .	8.0	0.0	12.0	20.5

Benzene,  $C_6H_6$ , and other aromatic hydrocarbons are distinguished from aliphatic hydrocarbons by the fact that they give nitro compounds and sulphonic acids when treated with concentrated nitric and sulphuric acids. Thus, benzene gives either mono- or dinitrobenzene and either its mono- or disulphonic acid very readily; the paraffin hydrocarbons are not acted upon by either acid. Not only do these hydrocarbons dissolve oils, but certain soaps also, particularly in the presence of dissolved fatty acids, such as oleic acid.

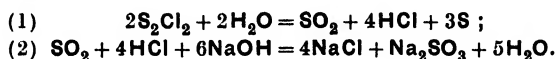
**Chlorinated Hydrocarbons.**—The simplest of these is *carbon tetrachloride*,  $CCl_4$ . It is made by passing a mixture of chlorine gas and carbon disulphide vapour through a heated tube, or by passing the chlorine into boiling carbon disulphide containing a little iodine:



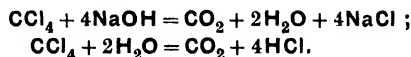
The sulphur dichloride, which is, like carbon tetrachloride, a liquid, is removed



by treating the mixture with sodium hydroxide and water, when the following changes take place:

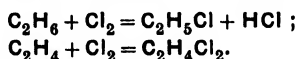


The carbon tetrachloride is then separated, dried, and purified by distillation. It is a colourless liquid, with a specific gravity of 1.631 and boiling at 76° C. It has a characteristic smell somewhat like that of chloroform, and like chloroform it has anæsthetic properties. Its vapour is non-inflammable. It is an excellent solvent, but is subject to one disadvantage: when its vapour is heated with a caustic alkali, or even with water, it is decomposed, with the formation of carbon dioxide and either sodium chloride or hydrochloric acid:



The tendency to decompose in the presence of water, with the liberation of hydrochloric acid, makes carbon tetrachloride liable to cause corrosion of metallic vessels.

The other chlorinated hydrocarbons used as solvents are derived chiefly from ethane,  $C_2H_6$ , and ethylene,  $C_2H_4$ . All of these are like carbon tetrachloride—definite compounds with a constant boiling-point. They are prepared by treating the hydrocarbons with chlorine under suitable conditions. The chlorethanes are substitution products, while the chlorethylenes are addition compounds. This is illustrated by the equations:



The following include the more important of these solvents, other than carbon tetrachloride:

	Boiling-point.
Dichlorethylene, $C_2H_2Cl_2$ . . . . .	52° C.
Ethylene dichloride, $C_2H_4Cl_2$ . . . . .	85° C.
Trichlorethylene, $C_2HCl_3$ . . . . .	87° C.
Perchloride of ethylene, $C_2Cl_4$ . . . . .	120° C.
Tetrachloride of ethylene, $C_2H_2Cl_4$ . . . . .	147° C.
Tetrachlorethane, $C_2H_2Cl_4$ . . . . .	144° C.
Pentachloride of ethane, $C_2HCl_5$ . . . . .	159° C.

These compounds are all non-inflammable, but have anæsthetic properties. They are all heavier than water, the specific gravity ranging from 1.25 to 1.7. They all have a tendency to decompose when heated with caustic alkalis or steam, in a similar manner to carbon tetrachloride. Ethylene dichloride is said to possess the greatest stability in this respect. Trichlorethylene and tetrachlorethane are sold under the proprietary names of *Westrosol* and *Westron* respectively.

*Chlorinated aromatic hydrocarbons*, such as *monochlorobenzene*,  $C_6H_5Cl$ , have also a limited use as solvents. Monochlorobenzene is a colourless liquid, heavier than water, with a boiling-point of 132° C. It is not decomposed by either steam or alkalis.

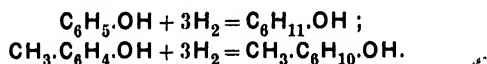
Chlorinated hydrocarbons can be distinguished from hydrocarbon solvents by their smell and by the fact that they are all heavier than water. If a few drops of the liquid are warmed gently in a test-tube with a clean shaving of

metallic sodium, the chlorine is changed into sodium chloride. If the residue is extracted with distilled water, made acid with nitric acid, and some silver nitrate solution added, a white precipitate of silver chloride is produced.

**Hydrogenated Aromatic Hydrocarbons.**—These are made chiefly from benzene and naphthalene. When the vapour of these bodies is mixed with hydrogen, and led over finely-divided nickel heated to a suitable temperature, the hydrocarbons absorb hydrogen, forming “hydrides,” the nickel acting as a catalyst. Benzene treated in this way gives *hexahydrobenzene* (cyclohexane, hexamethylene),  $C_6H_8.H_4$  or  $(CH_2)_6$ . This is a liquid with a specific gravity of 0.76 and a boiling-point of  $69^\circ C$ .

Naphthalene gives several hydrides. Two of them, the tetrahydride and decahydride, are used as solvents, the latter chiefly in the preparation of varnishes. *Naphthalene tetrahydride*, *tetralin*,  $C_{10}H_8.H_4$ , is a liquid with a smell similar to that of naphthalene. It is heavier than water, and boils at  $206^\circ C$ . Although an excellent solvent, its high boiling-point makes it rather difficult to recover, but, like many organic liquids, it volatilizes readily with steam.

*Hydrogenated phenols and cresols* are also known, and are used in the preparation of detergent soap solutions. *Hexalin* and *methylhexalin* (*J. Soc. Dyers Col.*, 1923, **39**, 365) are obtained by hydrogenating phenol and cresol respectively, and possess the characteristics of an alcohol with a high molecular weight. Their formation may be represented thus:



These solvents readily dissolve fatty-acid soaps (*i.e.* soaps mixed with free fatty acids), forming clear solutions possessing very marked detergent properties, dissolving calcium and magnesium soaps. It is said that with these solvents emulsions of hexalin soap and mineral oil, containing 50 per cent. of the latter, can be washed out of woollen goods in a few minutes at ordinary temperatures.

## CHAPTER XX.

### THE SCOURING AND BLEACHING OF SILK.

Raw silk contains, besides sericin, only traces of fat and mineral matter. It can be used in the raw state, and afterwards either boiled off or not, according to the purpose for which it is intended. But, generally, the silk-gum and other impurities are removed from the silk in the hank form by the process of *boiling off*. This depends upon the solubility of sericin in a hot solution of soap in water, to which, sometimes, a mild alkali, such as sodium carbonate, is added. If all the sericin has been removed, the product is *boiled* or *boiled-off* silk. If only part has been removed, either *souple* or *écru* silk is obtained. *Souple* silk is raw silk from which about 10 per cent. of the silk-gum has been removed, while in *écru* as little as possible—not exceeding 4 per cent.—is taken away, the object being rather to cleanse the skeins than to degum them. The process is similar for all three kinds, differing only in severity. With regard to *écru* silk, if raw silk is soaked in a 2 per cent. solution of formaldehyde and dried, it can be boiled without losing any weight.

**Boiling-off.**—In the boiling-off process, soft or softened water is essential. If hard water is used, calcium and magnesium soaps are liable to be deposited in the fibre. These cause both discolorations and uneven colours when dyed. If the silk itself contains either calcium or magnesium, it should be soaked in a bath of dilute hydrochloric acid (about 1 per cent.), and then washed thoroughly, first with water, then with a dilute solution of sodium carbonate or ammonia, and finally with water again.

About 25 per cent. of soap on the weight of the silk is used. Sometimes when hard water is employed, sodium carbonate is added to the bath. In such cases the best method of procedure is to boil the water in another vessel with sufficient sodium carbonate to precipitate the permanent hardness, then to allow the precipitate to settle, and to draw off the clear water. The soap used must be freely soluble. Those made from olive oil are the most suitable, and potash soaps are better than those made with soda, provided that they contain no free alkali. The soap having been dissolved in the water, the hanks are suspended in the solution from bent, frictionless rods. At first the temperature of the bath should be about 40° C. It is raised gradually to 90° or 95° C., the hanks being turned occasionally. Boiling the liquor or undue movement of the silk must be avoided, as it tends to make the threads stick together, and may also rupture the fibres, causing *flocons*, which subsequently cause trouble in dyeing. The sericin gradually becomes soft, then swells up, and finally dissolves in the soap solution, leaving the white threads of fibroin. After about half an hour the silk is removed to a second bath, made up in the same way as the first. At the end of half an hour it is transferred to a third soap bath to complete the solution of the gum.

These baths consist, generally, of rectangular vessels heated by means of steam. They are used continuously, till the first becomes saturated with sericin. It is then removed, and No. 2 bath becomes No. 1; No. 3 takes the place of No. 2; and a new bath of soap and water is made up in place of No. 3 (Fig. 115).

In this way the silk is boiled in baths each of which contains less gum than that preceding it. The saturated solution of sericin in soap and water is used in silk-dyeing under the name of *boiled-off liquor* or *bast soap*. It is a highly colloidal solution, and assists in the level deposition of the dye on the fibre. After the complete solution of the sericin, the silk is washed thoroughly with hot water to remove the soap liquor, and then dried.

Sometimes, after the silk has been removed from the soap bath, it is placed in canvas bags (to prevent tangling of the threads) and boiled in water containing a little sodium carbonate or soap, and then washed with hot water.

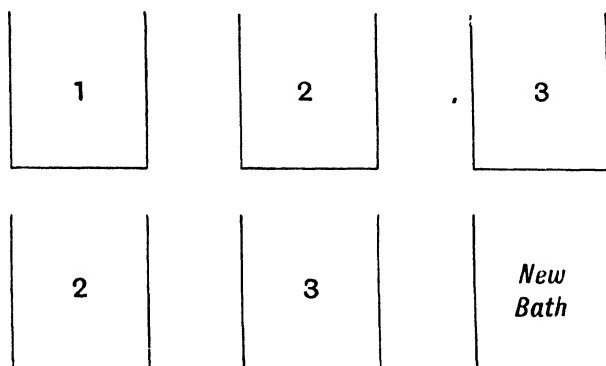


Fig. 115.—Baths for Boiling-off Silk.

But prolonged boiling is always liable to damage the fibre. Some kinds of silk are much more easily damaged than others. In such cases the use of soap baths containing much dissolved sericin has been found to be harmful, and fresh baths should be used for each lot of silk, at any rate in the first stages. Also, undue movement or rough handling must be carefully avoided, until most of the gum has been dissolved. The presence of free alkali in the soap is also a contributory cause of this kind of damage.

If scroop is required, the silk is soaked in a 0.5 per cent. solution of acetic or tartaric acid, and squeezed or hydro-extracted before drying.

The details of the process are subject to local variation. The following is an example of a somewhat simpler method of treatment:

For 20 lb. of silk make a bath of 80 to 120 gallons of water. After softening with a little sodium carbonate, dissolve 6 lb. of soap in the bath. The silk is worked in this bath for from three-quarters to one and a half hours at about 205° F. (96.1° C.). From 1 to 1½ lb. of silk is placed on each rod, and it is turned only once or twice during the boiling-off process. Yellow silk is treated for three-quarters of an hour in a second bath, which has a temperature of 205° F., and which contains only half as much soap as the first. The silk is then rinsed in a lukewarm bath of soft or softened water, and finally washed in cold water. The second soap bath is replenished by adding 3 lb. of soap, and is used for the next lot of silk.

Certain mechanical operations are necessary to develop the full lustre of the boiled-off silk. They consist of (1) stretching the hanks either by hand or by machine, (2) twisting them tightly and allowing them to remain thus for some hours, (3) smoothing or winding the silk on itself, and (4) steaming under tension. Water and sodium carbonate are used sometimes after the first soap bath, or even replace soap entirely. But silk should not be boiled in water containing more than one part of sodium carbonate per 1000.

Silk is often boiled off as piece-goods after weaving. Since raw silk has a greater elasticity and tensile strength than fibroin, weaving in the gum is less likely to cause damage, and weaker threads can be used. Further, the dirt accumulated during manufacture is removed also with the sericin. Materials made of mixed fibres are usually scoured in this condition. Piece-goods are boiled off by passing them at full width between rollers and through heated vats containing the soap liquor, and afterwards through hot water in a similar manner. Hose and half-hose are degummed in muslin bags to reduce friction.

The use of soaps whose fatty acids have a high titer or a marked smell must be avoided carefully. Sulphonated castor-oil or olive-oil soaps give good results; thus the use of a solution of turkey-red oil containing 25 g. per litre has been suggested. The formation of flocons is avoided chiefly by reducing movement and mechanical strain to a minimum. Many proposals have been made with this end in view. The following details are taken from an article by the authors in the *Silk Journal*, 1924, p. 32 (in U.S. Pat. 1,026,000—1912). The goods are sprayed in closed vessels with the hot soap solution. They are then subjected to the action of steam in the same vessel whilst still wet with the soap solution, and after this washed with water. The whole operation is carried out without moving the silk. The use of soap froth was patented by Schmidt Frères (Fr. Pat. 345,173—1904, from *J. Soc. Chem. Ind.*, 1905, **24**, 24) for the same purpose. Hot soap foam is produced by blowing compressed air into a heated soap bath. The silk is placed in a movable chamber above the bath, into which the foam rises. After about thirty-five minutes the sericin is dissolved, and the chamber is removed, and immersed in warm water to remove the soap and dissolved gum.

Colombo and Baroni (*J. Soc. Chem. Ind.*, 1911, **30**, 1445), who studied this method carefully, concluded that: (i) The froth method extracts the sericin as completely as the ordinary immersion process, but the silk loses rather less weight, because some of the soap remains in the boiled-off goods. (ii) The process is quicker than the old method. (iii) The effect of hard water is no greater. (iv) Like the ordinary method, the froth process is not so efficient when the fibre has been treated with soaps or fatty substances to facilitate working. (v) The strength and elasticity of the fibre are the same after both processes, as are also its behaviour towards dyestuffs and towards weighting agents. (vi) A better handle and lustre are produced, and there is far less likelihood of mechanical damage. Lorrain (Brit. Pat. 2359—1906) made use of soap froth for the simultaneous degumming and dyeing of silk. For example, 100 kilos of silk hanks are suspended in a vessel containing a solution of 33 kilos of soap and 5 kilos of rhodamine in 580 kilos of water. The silk is not in contact with either the solution or the walls of the vessel. The solution is heated to the boiling-point, and the lather rises and envelops the hanks. After thirty minutes' treatment with the lather the hanks are removed, and washed in hot water till free from silk-gum. This simultaneous degumming and dyeing was recommended strongly by a writer in the *Textile Recorder* for August, 1924. One of the chief difficulties encountered in the dyeing of silk

hosiery, such as stockings, is the unevenness of colour in the heels and toes. According to the writer in the *Textile Recorder*, this is due to the practice of degumming first and dyeing afterwards. If boiling-off and dyeing are conducted together by means of a soap bath or foam containing the dyestuff, the difficulty disappears entirely. A mixture of Turkey-red oil and sodium silicate is suggested instead of soap.

It is held by some chemists that the action of soap is injurious to the fibroin. Its use may be avoided by the American process, which consists in boiling the silk for half an hour under a pressure of 7 lb. in distilled water containing a small quantity of an alkali, such as ammonia, borax, or sodium carbonate, and then washing with water. Bayer & Co. patented an almost identical process (D.R.P. 301,255—1919). In this the raw silk is heated under a pressure of half an atmosphere in distilled water containing 0.25 per cent. of caustic soda. One would suppose, however, that this would be liable to produce flocons. The German patent D.R.P. 291,159 (1913) sought also to avoid, at any rate partially, the use of soap. The raw silk is impregnated with a solution of an alkali salt (other than soap) the acid of which is weaker than the amino acids of sericin, and then steamed. Sodium silicate, sodium borate, sodium stannate, and sodium aluminate are suggested. After steaming, which is said to separate the sericin from the fibroin, the former is dissolved by means of a soap bath or by soap foam from a boiling solution. In another process (D.R.P. 107,966—1917) a portion of the soap is replaced by galletamini, pelletes, or silkworm chrysalides. Nineteen parts of every twenty of soap can be replaced. Thus, a bath may contain 1 kilo of soap and 10 kilos of chrysalides. Goldschmidt (Brit. Pat. 131,906—1919) made use of the conjoint action of a peroxide or persalt and soap solution. Thus, for example, the silk is treated with a cold 0.1 per cent. solution of sodium peroxide and then boiled, without removing the peroxide, in a 0.2 per cent. solution of soap for from five to ten minutes. It is then rinsed and dried. Alternatively, the silk may be wetted with a 10 per cent. solution of hydrogen peroxide, and then boiled for from ten to fifteen minutes in a soap bath.

In the patented process of Voigt and Buschhüter the silk is degummed by saturating it with a solution of an alkali salt of a weak acid (e.g. sodium carbonate), and then steaming and washing. The addition of 0.5 g. of Monopol soap per litre is an advantage. After steaming, the silk is rinsed in cold water, and washed in a bath of hot soap and water.

Experiments made by Ristenpart (*J. Soc. Chem. Ind.*, 1918, **37**, 649A) showed that the degumming action of the sodium carbonate depends upon the proportion of soda to silk, and also on the concentration of the solution. For any given concentration of soda solution a certain minimum of alkali must be present to effect complete degumming, and the presence of an excess has no useful result. With decreasing concentration of soda, the minimum quantity required for degumming decreases also. Thus, for a concentration of 1 per cent. of sodium carbonate the minimum quantity of soda required lies between 1.64 and 2.35 per cent. of the weight of the silk, for 0.5 per cent. concentration between 0.85 and 1.63 per cent., and for 0.2 per cent. concentration between 0.54 and 1.0 per cent. On the large scale, centrifuges are used, and the quantity of soda required depends on the amount left in the goods after centrifuging. If the silk is centrifuged till it retains twice its weight of solution, the concentration of the latter should be 1 per cent.; if 2.5 times its weight is left, 0.5 per cent.; and if 3 times its weight, 0.2 per cent. These variations are explained by the increased hydrolytic dissociation of the sodium carbonate

into bicarbonate and hydroxyl ions which takes place with decreasing concentrations. The extension of the principle is limited by the danger of uneven saturation when larger quantities of liquor are left in the goods. Since only the quantity of soda necessary to combine with the sericin is used, there is no danger of the fibroin being attacked, and all traces of alkali are removed by washing.

Sericin is comparatively readily changed into soluble degradation products by proteolytic enzymes. Fibroin, although decomposed ultimately, is not attacked as long as the protective sheath of sericin remains. Thus, the action of these enzymes could, if controlled carefully, be stopped at the point where the sericin was just dissolved, leaving the fibroin unattacked. This process has been patented by Röhm and Haas (Fr. Pat. 475,343—1914): the silk is digested for some hours at 40° C. in a solution of 0.05 per cent. of pancreatin and 0.10 per cent. of soap, making the reaction of the mixture faintly alkaline by means of a weak alkali salt. After the digestion is complete, the silk is heated in water at 90° to 100° C. for about thirty minutes to complete the dissolution of the sericin, and then washed.

**Damage due to Degumming.**—The authors (*J. Soc. Chem. Ind.*, 1936, 55, 325r) made comparative tests of different methods of degumming, in which the product was examined by the zinc-chloride viscosity method (Table XLII). The deleterious action of sodium carbonate is very marked, and of interest, having regard to the fact that it is often used. Some varieties of silk contain a considerable amount of mineral matter, which may exceed 2 per cent. In such cases degumming should be preceded by a bath of hydrochloric acid the pH of which is that of the iso-electric point, after which the silk is washed thoroughly with water.

TABLE XLII.—DAMAGE DUE TO VARIOUS METHODS OF DEGUMMING.

Method of Degumming.	Viscosity.
Ungummed . . . . .	3.1
Olive-oil soap . . . . .	3.1
Olive-oil soap and 1 per cent. sodium carbonate . . . . .	2.0
5 per cent. Monopol soap and 2 per cent. sodium metasilicate . . . . .	2.95
Digestion with 0.1 per cent. pancreatin and 0.1 per cent. soap . . . . .	2.52

**Souple Silk.**—For this about 10 per cent. of soap is used, and only one bath is necessary. The temperature of the latter is maintained at about 40° C., or just hot enough to soften the sericin without actually dissolving it. As soon as the gum is softened, the silk is removed from the bath, and washed. Souple silk generally retains the colour of the raw silk, and hence is suitable only for dark colours or heavy shades. It is rather harsh in feel, but is softened by soaking in a warm 0.5 per cent. solution of cream of tartar (potassium hydrogen tartrate), and washing. Sodium bisulphite, sulphurous acid, and sodium bisulphate act in the same manner.

**Écru.**—The raw silk is simply washed in lukewarm weak soap solution containing about 1 part of soap to 100 of water.

**Chappe silk** is stripped when necessary by heating it to about 205° F. (96° C.) for an hour in a solution of sodium carbonate containing about  $\frac{1}{4}$  lb. for each

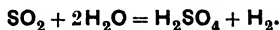
10 lb. of silk. It is then treated in a second bath containing 3 lb. of soap for 10 lb. of silk.

**Determination of Amount of Silk-gum, or Loss on Boiling off.**—From 3 to 5 g. of the sample is dried in the drying-oven, and weighed in a stoppered weighing-bottle. The dry silk is then boiled gently for about an hour in a 1 per cent. solution of olive-oil soap. It is then squeezed, and transferred to a second beaker containing a 1 per cent. solution of sodium carbonate. After boiling in this solution for about half an hour, the silk is washed thoroughly with hot distilled water, dried in the oven, and again weighed in the stoppered weighing-bottle. The loss in weight is due to the silk-gum, and is calculated to a percentage.

### The Bleaching of Silk.

It is not always necessary to bleach silk. In the case of silk which has to be dyed black or a dark colour, for example, it would be a waste of time. Moreover, since silk loses nearly all of its natural colour with the removal of the sericin, leaving a nearly white residue of fibroin, bleaching is rarely necessary for boiled-off silk unless it has to be dyed in light shades or bright colours, or white silk is required. The bleaching agents used for silk are sulphur dioxide or sulphurous acid, bisulphites, hydrogen peroxide or sodium peroxide, and potassium permanganate.

**Bleaching with Sulphur Dioxide.**—This process is commonly called *stoving*, or, more simply, *bleaching with sulphur*, from the fact that the sulphur dioxide is made as required by burning sulphur in a stove. The bleaching chamber, or stove, is a rectangular brick chamber lined with wood, lead, glass, or tiles. No metal that would be attacked by acid is used in its construction. The hanks or skeins of silk are hung on wooden pegs or bars in the chamber. They must be damp, but should not contain enough water to trickle down and drip from their lower ends. The chamber is filled with sulphur dioxide. Sometimes sulphur is placed in pots in the chamber, and ignited; in other cases it is burnt in a stove connected with a pipe which opens beneath perforated tiles forming the floor of the chamber. When the sulphur is burnt in the bleaching chamber there is a danger of some of it volatilizing and becoming deposited on the goods. There is less likelihood of this happening if it is burnt outside, and the gas delivered into the chamber. From 5 to 7 lb. of sulphur is used for 100 lb. of goods. When the chamber is full of sulphur dioxide, it is closed and left for some hours. The presence of moisture is necessary, since sulphur dioxide bleaches by liberating hydrogen from water:



The hydrogen bleaches by reduction. It does not, unlike an oxidizing bleaching agent, break up the colouring-matters into simpler or soluble colourless compounds, but is thought to combine with them, forming white or colourless bodies which are termed *leuco compounds*. In addition, the silk adsorbs, and combines with, both the sulphur dioxide and the sulphuric acid. A great deal more sulphur dioxide disappears than is necessary simply to combine with the colouring-matters, and without this excess there is no bleaching action.

The chamber is next opened, and the unused sulphur dioxide blown out with a current of air. The silk is then taken out, and washed thoroughly with water to remove the sulphurous and sulphuric acids. If it is not bleached



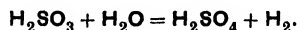
sufficiently, the process is repeated. The leuco compounds which are formed are not washed away. Part of them, at any rate, remain in the silk. When the bleached silk is exposed to air, the hydrogen of the leuco compounds is gradually oxidized, and the original colour reappears. In order to correct or neutralize this tendency to *yellowing*, goods bleached with sulphur dioxide are generally *tinted* or *died white* with a small quantity of a coal-tar dye. Methyl violet or acid violet are commonly used for this purpose. Not more than 0.005 per cent. on the weight of the silk is required; it may be applied by soaking the silk in a bath of water containing a little soap, together with the dissolved dyestuff, or in a bath of water alone. As the original yellow colour of the silk is reproduced, its effect is neutralized by the dyestuff, and the goods still appear white to the eye.

Since silk is damaged by sulphurous or sulphuric acid if allowed to dry into it, it is very important to wash it thoroughly after stoving. A bath of very dilute mild alkali would neutralize the acid and make it easier to wash away, but if stoved goods are treated with alkaline solutions the yellow colour quickly reappears.

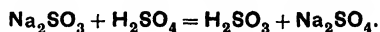
Instead of burning sulphur to obtain sulphur dioxide, a cylinder containing the liquefied gas may be used. But it is a curious and hitherto unexplained fact that ready-prepared sulphur dioxide is not so effective a bleaching agent as that made on the spot from burning sulphur. The same remarks apply also to sodium sulphite or bisulphite, though the latter is sometimes used. It is possible that the explanation may be that sulphur dioxide made by burning sulphur always contains traces of sulphur trioxide,  $\text{SO}_3$ . In order to bleach silk with sodium bisulphite, about 25 per cent. on the weight of the goods is dissolved in water. This gives rise to a solution of sulphurous acid and sodium sulphite:



The silk is wetted down, and soaked for about twelve hours in this solution. The sulphurous acid acts, of course, like sulphur dioxide:



The silk is removed from the bath and squeezed. It is then put into a bath of dilute sulphuric acid of about 5° Tw. specific gravity. This decomposes the sodium sulphite remaining in the goods, and causes a further bleaching effect:



After soaking in the acid bath, the bleached goods are washed and tinted in the same way as after the stoving process. In both cases scroop may be imparted to the fibre by the process already described.

**Bleaching with Hydrogen Peroxide.**—The chemistry of the bleaching bath has been explained already. There are, however, certain essential conditions which must be remembered. Before bleaching, the goods must be thoroughly scoured to ensure that they are completely permeable. Residues of unremoved sericin or calcium or magnesium soap must be particularly avoided. Any trace of iron or other metal which could act as a catalytic agent must also be guarded against. Nothing but soft water must be used in making up the bleaching bath.

The bleaching vat should be made of wood, slate, porcelain, glazed bricks or stainless metal. A suitable vat, recommended by the Castner-Kellner Alkal

Co., Ltd., is shown diagrammatically in Fig. 116. It is heated by means of a lead steam coil, placed beneath a false bottom, entering at one end, coiling backwards and forwards, and finally going out at the other end of the vat. An open steam pipe should never be used. The false bottom above the steam pipe prevents the goods from becoming entangled with the pipe, and allows any solid suspended matter in the liquor to settle out. A movable perforated top is provided which can be fixed just below the surface of the liquor, thus ensuring that the goods are completely immersed. For piece-goods a suitable dolly or jigger may be used.

*Preparation of the Bath.*—For each 10 lb. of silk about 20 gallons of liquor are required to allow of adequate room for circulation. If ten-volume hydrogen peroxide is diluted with four times its volume of water, a two-volume peroxide solution is obtained. About 20 gallons of this should be sufficient for each 10 lb. of silk to be bleached. The diluted peroxide is placed in the bleaching

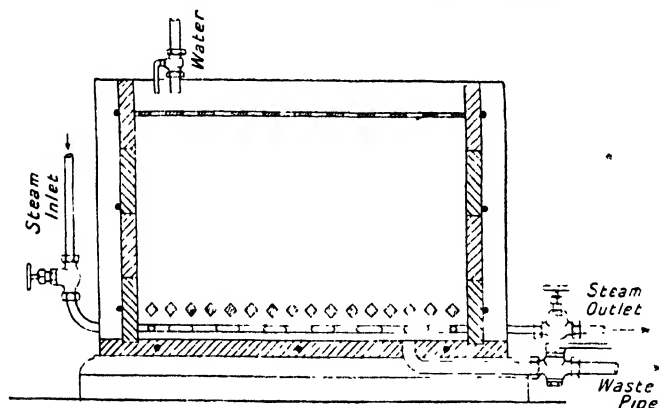


Fig. 116.—Castnor-Kellner Bleaching Vat.

bath, and its reaction is tested. The solution should be faintly acid to litmus-paper or, better, to phenol red. The test may be made by spotting drops of phenol-red solution on a porcelain plate, withdrawing a drop of the liquor from the bath by means of a glass rod, and mixing it with one of the drops of the indicator. In the presence of acid a yellow colour is produced. If the reaction is not acid, a little dilute sulphuric acid is stirred in till a slightly acid liquor is produced. When softened water is used for making up the bath, sodium carbonate may be present, which will neutralize the acidity of the original peroxide. It is very important to have no unconsidered alkali in a peroxide bath.

The faintly acid solution is next neutralized carefully with either diluted ammonia, sodium silicate, or sodium phosphate. Magnesia, made into a cream with water, may also be used. Great care must be taken to avoid a large excess of alkali. While the reaction of the bleaching bath must be just alkaline, excess of alkali makes the peroxide unstable, causing it to decompose too rapidly and the oxygen to escape without exercising any bleaching action. Again, phenol red is the best indicator to use, the alkali being added till a drop of the liquor just produces a red colour but no colour with phenolphthalein. Ammonia and sodium silicate are the alkalis most commonly used. According to Weber (*J. Soc. Dyers Col.*, 1923, 39, 212), sodium silicate is preferable to ammonia from the point of view of economy of oxygen. He found that while

even small quantities of free ammonia caused a considerable loss of oxygen at 100° F. (37·8° C.), with equivalent quantities of sodium silicate, under the same conditions, the loss was negligible. The only objection to sodium silicate is that if too much is used the goods acquire a harsh feel.

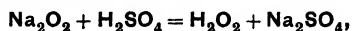
The addition of a little borax or magnesia is advantageous with goods which are difficult to bleach, and for which a comparatively high temperature is helpful. The stability of magnesium hydroperoxide has already been referred to. Borax acts in a similar manner owing to the formation of perborates in the bath. The addition of an excess of sodium silicate over that required for neutralization also gives an increased stability.

After neutralizing the bath, a little Turkey-red oil or soap, previously dissolved in water, may be added to assist penetration. About half a pound to 20 gallons of liquor is sufficient.

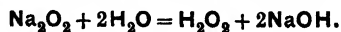
The goods are wetted down, squeezed, and introduced into the bath. The temperature is raised to from 100° to 120° F. (38°–49° C.), the steam shut off, and the lid put into position. The goods are turned occasionally during the next six hours, and are commonly left in the bath overnight. Next morning the excess liquor is squeezed back into the bath, or centrifuged out and returned. The silk is then washed and scrooped in the usual way. If magnesia has been used, a bath of dilute acid is necessary before washing, in order to free the silk from any magnesia which has become deposited on the fibres.

The residual hydrogen peroxide in the bath is estimated by titration with potassium permanganate in the manner already described. Sufficient hydrogen peroxide solution is added to bring the bath back to its original strength, and, after its reaction has been adjusted, it may be used again. Hydrogen-peroxide bleaching is followed sometimes by stoving, or by a bath of sodium bisulphite. The more concentrated form of hydrogen peroxide (100-volume) has advantages. In particular, it makes it possible to strengthen up old baths without much dilution. When a bath is not used again quickly, loss of hydrogen peroxide may be prevented by making it faintly acid with sulphuric acid.

**Bleaching with Sodium Peroxide.**—A solution of hydrogen peroxide can be prepared as required by dissolving sodium peroxide in water or dilute sulphuric acid. From the equation:



the quantity of acid necessary for liberation of the hydrogen peroxide is calculated, 78 parts of sodium peroxide requiring 98 of sulphuric acid. Thus, each part of sodium peroxide needs about 1·3 of acid. In order to make a bleaching bath of two-volume hydrogen peroxide there would be required (i) 6·88 lb. of sodium peroxide and (ii) 7·94 lb. of sulphuric acid (or in round numbers, say 6½ lb. and 8 lb. respectively) for each 50 gallons of bleaching liquor. The sulphuric acid is mixed with about 30 gallons of cold water in the bleaching bath, and the sodium peroxide is stirred in slowly. When the peroxide has dissolved completely, the reaction of the bath is tested with litmus-paper. If it is alkaline, this means that insufficient sulphuric acid has been used, and some free sodium hydroxide is present:



Caustic alkali must never be present in a bleaching bath. Dilute sulphuric acid must be stirred in till the reaction is faintly acid to litmus-paper. Then, since an acid bath is not sufficiently unstable, a mild alkali, such as ammonia or a solution of sodium silicate, is added till the reaction is faintly alkaline to

phenol red. Some soluble oil, such as Turkey-red oil, or a freely soluble soap previously dissolved in hot water, may be added, if desired, or a little magnesia if the bath is to be heated to a high temperature.

When making up sodium-peroxide liquors, it must be remembered that a considerable amount of heat is evolved when this substance dissolves in water, which may cause loss of hydrogen peroxide. It is an advantage to make up the solution in a separate tank, raised to such a position that the solution can be run into any one of the bleaching vats by means of a rubber hosepipe. The Castner-Kellner Alkali Co. recommend the use of a round wooden tank, built up like a barrel (or its top half), the only fastenings being the external iron hoops, which may be hammered downwards to prevent leakage. A round form of dissolving tank has no dead corners where undissolved sodium peroxide can settle. The tank should be fitted with a mechanically-driven wooden stirrer and two run-off cocks of wood or earthenware, one about 2 or 3 inches above the bottom to run into the bleaching vat, and the other right at the bottom to run to waste. The bottom of the vessel should slope towards this waste cock. Hydrochloric acid has advantages over sulphuric acid, since it develops much less heat when diluted with water; but it must be free from iron. The water required should be run into the dissolving tank, and acid added in the proportion of  $9\frac{1}{2}$  lb. of hydrochloric or  $12\frac{3}{4}$  lb. of sulphuric for each 10 lb. of sodium peroxide. The diluted acid is then allowed to cool. The sodium peroxide is sprinkled slowly into the acid with constant stirring, but violent agitation must be avoided, as it tends to decompose the hydrogen peroxide. The temperature must not be allowed to rise, and any sodium peroxide which floats on the surface must be immediately immersed. The bath should be stirred slowly for about ten minutes after all the peroxide has been added. The reaction is then tested, and made faintly acid if necessary. The strength of this stock solution is determined by titration, and sufficient of it is run into the bleaching bath to give a one- or two-volume hydrogen peroxide as required. The bleaching process is then carried out exactly as with a hydrogen-peroxide bath.

The following are examples of sodium-peroxide bleaching baths which have been recommended:

(1) For 100 lb. of silk use  $7\frac{1}{2}$  lb. of sodium peroxide, 10 lb. of sulphuric acid, 5 lb. of sodium silicate, and 0.5 to 10 lb. of soap made up to 100 gallons.

(2) For each 10 lb. of silk use, for a strong bleach, 5 lb. of sodium peroxide,  $4\frac{1}{2}$  lb. of sulphuric acid ( $168^{\circ}$  Tw.),  $4\frac{1}{2}$  gills of sodium silicate,  $1\frac{1}{2}$  lb. of soap, and 15 gallons of water. For a weaker bath from one-third to two-thirds of these quantities are taken.

When magnesia is used, the process may be simplified considerably by stirring the peroxide into a cold solution of magnesium sulphate; or the peroxide and Epsom salts are dissolved separately, and the solutions carefully mixed. At least 3.25 lb. of Epsom salts must be used for each pound of peroxide. It is essential that there should be a slight excess, or free sodium hydroxide may remain.

Mudford (*J. Soc. Dyers Col.*, 1926, 42, 45) uses 5 parts of 20-volume hydrogen peroxide and 1 part of sodium silicate ( $70^{\circ}$  Tw.) in 200 parts of water. The bath is raised to the boiling-point and the degummed silk is entered and allowed to remain in the bath for 1 to  $1\frac{1}{2}$  hours. Soap may be added if desired.

After bleaching with sodium peroxide, the liquor is squeezed back into the bath, and the goods are washed, first with warm and then with cold water.

It is an advantage to use a dilute acid for the first wash, *e.g.* cold 0.1 per cent. hydrochloric or sulphuric acid, or a warm solution of oxalic acid.

**Bleaching with Potassium Permanganate.**—Good results can be obtained by the following method:

The silk is wetted down, and soaked in a cold 0.1 per cent. solution of potassium permanganate containing also the same proportion of sulphuric acid. After about six hours it is removed, rinsed, and passed into a bath of sulphurous acid of about 1° Tw. When the oxides of manganese have been completely dissolved, the silk is removed and washed. A better white is obtained if a dilute acidified solution of hydrogen peroxide is used instead of sulphurous acid, although, of course, this makes the process more expensive.

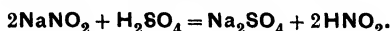
**Bleaching of Souple Silk.**—When the gum has to be bleached, aqua regia, nitrous acid, and nitrosylsulphuric acid (chamber crystals) are sometimes employed, although they are admitted to be unsatisfactory in their action.

*Aqua regia* is made by mixing 5 parts of commercial hydrochloric acid of 32° Tw. with 1 part of nitric acid of 61° Tw., and allowing the mixture to stand for about five days at 20° to 25° C. The solution contains a mixture of nitrosyl chloride, NOCl, and chlorine:

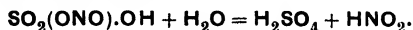


Before use this solution is diluted to a density of 4° Tw. The silk is steeped in the diluted aqua regia at ordinary temperature, until it has acquired a greenish tint. It is then removed, and washed till the green colour disappears. If it is left in the aqua regia too long, a yellow colour is produced, and this is not removed by washing.

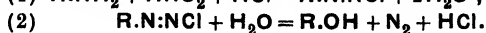
Nitrous acid is used in a similar manner. It is prepared as required by adding sulphuric acid to a solution of sodium nitrite:



Nitrosylsulphuric acid when dissolved in water gives also a solution of nitrous acid, in accordance with the equation:



In either case a cold bath of about 4° Tw. specific gravity is employed, the silk being immersed in the bleaching liquor for from ten to fifteen minutes, and then washed thoroughly with cold water. These bleaches are very uncertain in their action, since secondary reactions take place. When aqua regia is used, the chlorine attacks the sericin and fibroin, with the formation of chloramines of the general formula  $\text{R.NHCl}$  or  $\text{R.CO.NHCl}$ . The production of a yellow colour indicates the presence of these compounds. The combined chlorine can be removed by means of a bath of sulphurous acid, but the damage done to the fibre cannot be repaired. Nitrous acid reacts with the free amino groups, giving rise to azo compounds, which have in the case of silk a yellow colour, and are decomposed when dried, giving rise to deaminated silk, which has a brownish tint. These reactions are expressed thus:



It is obvious that these secondary reactions form grave objections to the use of either of these bleaching agents. Hence, stoving is made use of whenever possible.

*Sodium perborate*,  $\text{NaBO}_3.4\text{H}_2\text{O}$ , is recommended by the Castner-Kellner Alkali Co. for bleaching all kinds of silk. The sodium hydroxide liberated

must be neutralized by the addition of the requisite quantity of acid, sodium bicarbonate, or sodium phosphate. The bath is then used in the same way as one containing hydrogen peroxide.

**Tussur and other wild silks** require special treatment. Tussur silk, in particular, is so difficult to bleach that it is commonly used in its natural fawn colour. It was noted above that it is much more resistant to chemical reagents than ordinary silk. It can be boiled with a comparatively strong solution of sodium carbonate without being damaged. Bleaching agents can be used also under conditions which would be impossible with ordinary silk. In boiling off, about 5 per cent. of sodium carbonate and 10 to 15 per cent. of soap may be used, and the temperature kept at the boiling-point for from one-and-a-half to two hours. At least two such boilings are required to remove the gum. After this the silk is washed, and bleached with hydrogen peroxide. Sulphur dioxide will not bleach Tussur silk. Even peroxide has little action at the ordinary bleaching temperature, but if sodium silicate or magnesia is used the temperature may be raised gradually to the boiling-point. Potassium permanganate is more efficient than peroxide, though it is seldom used. The following example shows the type of bleaching bath employed:

For 10 lb. of the silk from 1 to 1½ gallons of ten-volume peroxide is taken and suitably diluted. The acidity is neutralized with sodium silicate solution, and a further quantity of about 1 lb. for each gallon of peroxide is then added. The silk is wetted down and introduced into the bath, and the temperature is raised gradually to the boiling-point.

Sodium perborate, on account of its comparative stability, is also suitable for bleaching Tussur silk. Friedmann (*J. Soc. Chem. Ind.*, 1912, **31**, 770) recommends the following process:

(1) *Degumming* is carried out with a solution of 10 lb. of coconut-oil soap, containing 10 per cent. of benzene dissolved in 100 gallons of water to which 2 lb. of sodium perborate dissolved in cold water is added; the silk is introduced, and the temperature of the bath is raised gradually to 160° F. (71·1° C.), and maintained at this temperature for from three to six hours. After this the degumming is repeated in a fresh bath of the same composition, and the silk is then washed.

(2) *Decolorizing*. The degummed silk is treated with six- to ten-volume hydrogen peroxide at 105° F. (40·6° C.), made faintly alkaline with ammonia. It is then washed in water, soaked in a 0·1 per cent. solution of oxalic acid at 160° F. (71·1° C.) for four hours, and again washed.

(3) *Final bleach*. After the peroxide treatment the goods are immersed in a 0·1 per cent. solution of sodium hyposulphite at 85° F. (29·4° C.) for twelve to twenty-four hours. They are then washed and dried. Pokovny (*J. Soc. Dyers Col.*, 1926, **42**, 129) recommends the use of alcoholic hyposulphite, viz. 100 g. of hyposulphite, 2 litres of alcohol, and 600 ml. of water. Another process consists in padding with a 5 per cent. solution of sodium sulphonylate, then steaming for 5 minutes, and afterwards soaping and washing.

## CHAPTER XXI.

### THE SCOURING AND BLEACHING OF WOOL.

THE impurities which have to be removed from wool are much more complex than is the case with silk. Raw wool contains: (i) wool fat, (ii) dried perspiration or suint, (iii) dirt, and (iv) vegetable débris.

Most of these are removed before spinning, but during spinning and weaving or knitting, oil and soap are used as lubricants, while considerable quantities of dirt are also picked up. All of these must be removed as completely as possible before the wool can be either bleached or dyed.

The suint is soluble in water. The dirt cannot be removed till the fat which causes it to adhere to the fibre is set free; the vegetable débris or burrs can be got rid of only by carbonization. The purification of raw wool involves three distinct types of processes: (i) removal of suint by solution in water; (ii) removal of fat and liberation of dirt, followed by the washing away of the latter; and (iii) carbonization of vegetable matter. The suint and wool fat are valuable by-products, the former serving as a source of potash, while lanoline is prepared from the latter.

There are three ways in which oil or fat may be removed from textile fibres or goods: (i) by saponification, and washing out with water the soluble soap produced; (ii) by emulsification with a solution of soap; and (iii) by solution in an organic solvent.

*Saponification* involves boiling the goods with a solution of caustic soda, and is, therefore, unsuitable for wool or other animal fibres, though it is applied to cotton. The *emulsification* process is almost entirely used for wool. It does not damage the fibres, but has certain disadvantages. It is very difficult to remove the fat completely as an emulsion, and wool has the property of adsorbing soap from its solution, which makes it extremely difficult to free the goods from it.

**Solvent Process.**—The organic-solvent process is capable of removing the whole of the oil or fat, and does not introduce any other impurity such as soap. From a chemical point of view it is far superior to the emulsification process. In practice it is attended with some difficulties, such as the necessity for special plant and the use of inflammable liquids. These difficulties have tended to prevent the general adoption of the method, together with the idea that it gives the wool a harsh feel. The last objection, however, is due chiefly to prejudice.

The chief advantages of the solvent method are summarized by Hey (*J. Soc. Dyers Col.*, 1920, 36, 11). They are—

- (1) The solvent has no injurious effect on the fibre.
- (2) Both the oil and the solvent are easily recovered.
- (3) Cloths and yarns for dyeing need not in most cases be treated with water before dyeing.

- (4) All the grease and most of the dirt are removed.
- (5) The goods are left in the best possible condition for subsequent processes.
- (6) Any soaping necessary to remove residual dirt need be of only a very mild character, water alone being sufficient in most cases.
- (7) Better results are obtained in bleaching.
- (8) If other oils have to be used in weaving, it is better to start with oil-free goods.
- (9) There is no danger of shrinkage, felting, or of alkali damage.

The only difficulty in connection with the solvent process is the removal of the dirt and suint, though Hey states that if the goods are not packed too tightly in the extracting chamber the dirt is washed away with the grease by the solvent. But the suint would still remain. Hence, as a general rule, both suint and dirt must be removed, after degreasing, by washing with warm water. This introduces a further difficulty, though it is one which is easily controlled. No solvent must be present in the wool when it is washed with warm water, or emulsions are formed which are very difficult to deal with.

Hey (*loc. cit.*) gives the following explanation of the action of the organic solvent upon the grease and dirt: All materials exposed to air become coated with condensed moisture. This resists the action of the solvent, and the object of solvent scouring is to remove this film of water from the surface of the goods in a manner similar to that of ordinary wet scouring, *i.e.* by emulsification, in order that the dirt may be liberated. Soaps which are soluble in water do not, as a rule, dissolve in organic solvents, but oleates do, in the presence of excess of oleic or other fatty acid. Such a solution of soap in organic solvent dissolves the grease, and the soap takes up the film of water and emulsifies it. Thus both the grease and the dirt are removed. In soap scouring, the emulsification is that of oil in water, in organic-solvent scouring that of water in solvent. The water breaks up into minute drops, which, together with the dirt, remain suspended in the form of an emulsion, and are carried away by using two or three baths. The emulsions of water in solvent are not so stable as those of oil in water, since the surface tension is not lowered to the same extent.

The organic solvents which may be used have been described already. The apparatus employed must include an extraction chamber and a still for the recovery of the grease and solvent. The process may be either intermittent or continuous. The principles are illustrated by the types of extractors used for extracting small quantities of material in a laboratory.

(1) *Intermittent Process.*—The stoppered funnel (Fig. 117) is filled with the wool. The tap is closed, and petroleum ether is poured into the funnel till the wool is covered with the solvent. The stopper is replaced, and the apparatus allowed to stand for some hours. The stopper is then removed, the tap opened, and the solvent allowed to run out into a flask. After it has drained completely the tap is closed, and the extraction repeated. After about four extractions the wool will be free from fat.

(2) *Continuous Process.*—This enables a small quantity of the solvent to extract a large amount of the material. There are two types of continuous-extraction apparatus:

*Lloyd's continuous-extraction apparatus* is suitable for all kinds of textile experiments. It has the advantage of enabling the extraction to be carried



Fig. 117.—  
Separating-  
funnel.



out near the boiling-point of the liquid solvent. The apparatus is illustrated in Fig. 118, together with alternative forms of inner tubes. The simpler forms, such as *C*, are quite suitable. The tube *C* is either an air or water condenser, according to the boiling-point of the solvent.

The tube *A* has some glass points *p* fused on to the outer surface in order to allow the passage of the vapour. Some cotton-wool is placed at the bottom

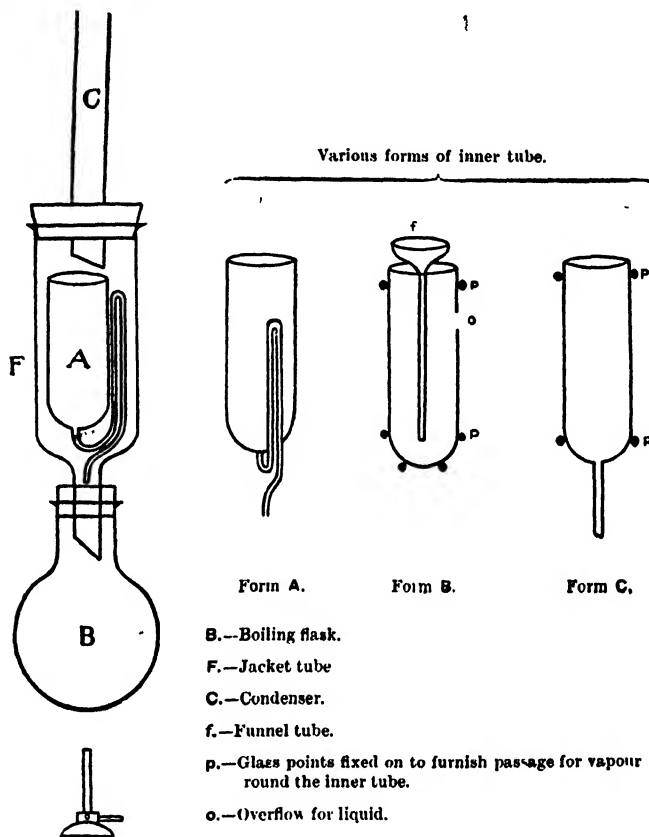


Fig. 118.—Lloyd's Extraction Apparatus.

to act as a filter and to regulate the flow of the solvent. The orifice and packing should be adjusted so that the condensed solvent accumulates, forming a head above the material which is being extracted. The apparatus described is that recommended by A. G. Green (*Analysis of Dyestuffs*, p. 81). The wool is placed in the tube *A*, and the solvent in the flask *B* is boiled gently either by means of a Bunsen flame or on a water-bath. The vapour passes up the space between the inner and outer tubes, condenses in the condenser, and the liquid solvent drops into the extractor, from which it finds its way again into the flask *B*. If, at the end of the extraction, the solvent is evaporated off, the residual fat in the flask may be dried and weighed.

**Soxhlet extractor.** The second type is illustrated by the Soxhlet extractor (Fig. 119). The wool is placed in the extraction chamber *C*, and the extractor

is then connected with a flask, containing the solvent, and a reflux condenser. When the flask is heated, the vapour of the solvent passes through the wide tube on the left and into the condenser. As it condenses it drops into the chamber, where it accumulates till it reaches the top of the siphon on the right. It then runs back into the flask, and the operation recommences.

The principles of industrial processes are the same as those described above, with one difference. When a small quantity of wool is extracted in the laboratory, the solvent remaining in the material after extraction is lost. When the operation is performed on an industrial scale, the loss caused in this way would be so great as to make the process too expensive to use; hence provision must be made for distilling off and condensing this solvent. A current of hot non-inflammable gas, such as carbon dioxide or steam, or centrifuging may be used for this purpose.

A very simple method is that of the Arlington process (*J. Soc. Dyers Col.*, 1921, 37, 235), in which a keir of 1000 lb. capacity is used. This is packed with the goods, filled with naphtha, and closed. After solution of the grease, the solvent is run off, and that remaining in the goods washed out with hot water. The keir is then opened, and the goods are unpacked and washed. In order to free wool completely from grease the extraction would have to be repeated at least three times, and this would make the process rather costly, since a large volume of solvent would be required, and it must be redistilled each time. This process is practically that of the experiment with the separating-funnel described above. Jacques (*J. Soc. Chem. Ind.*, 1900, 19, 48) uses a somewhat similar method. The wool is fed in the form of flocks on to a series of endless belts placed one above the other, and revolving in opposite directions in a tank containing the solvent. The wool moves through the solvent in the opposite direction to the flow of the latter, and is collected in another vessel. The excess of solvent is driven out in a vacuum or by a stream of hot water followed by one of hot air.

According to Hey (*J. Soc. Dyers Col.*, 1921, 37, 15), Smith's system of degreasing is very satisfactory. The apparatus consists of an outer iron casing to contain the solvent, and an inner steel case with a periphery of perforated plates to hold the material to be extracted. The cage is carried on a strong steel shaft, and can be made to revolve in the solvent at any desired speed. It is divided radially into four compartments, each with a door at the periphery, which can be brought opposite to another in the casing. The construction of the machine enables centrifuging to be done much more efficiently than with an ordinary hydro-extractor. Valves and pipes are arranged connecting the extracting chamber with storage tanks for clean, grey, and dirty solvent. The drying arrangement consists of large pipes, or ducts, leading from the top of the machine to a cooler, and then through a centrifugal airtight fan to a heater, and from this to the centre of the apparatus, where the hot gases are distributed through the material in the drying process.

The material is placed in the cages through the outer door of the casing. This is then closed and made airtight, the pressure is reduced by means of a pump, and the hot solvent is run in. Inert gas, such as carbon dioxide, is then led in till atmospheric pressure is reached. The cage is then rotated slowly in the solvent for a sufficient time to dissolve the grease. It is then stopped,

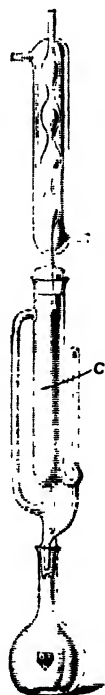


Fig. 119.—  
Soxhlet Ex-  
tractor.

and the outlet valve connected with the dirty tank is opened. The solvent runs away, and an equivalent volume of inert gas is drawn in through the delivery pipes and from the dirty storage tank. The machine is then run at high speed to remove the solvent as completely as possible by centrifugal action. The lower valve of the storage tank is closed, and, if necessary, the operation is repeated with fresh solvent. The drying is carried out by starting the fan, which circulates the inert gas through the heater, the materials in the machine, and the condenser. The condensed solvent is collected in a receiver or run direct to the storage tank. The drying is continued until the absence of solvent at the sight-glass shows that the material is dry. The doors are then opened and the goods removed in a hot, dry condition, or they may be first cooled by a current of cold gas. The impure solvent can be used again or pumped to the still for purification, and the distillate returned to the clean storage tank. The dirty solvent can be drawn up to the still by means of the vacuum-pump, and that in the vacuum receiver removed by a special ram pump attached to and worked by the vacuum-pump. Any variation of

pressure in the system is compensated or adjusted by the egress or ingress of the atmosphere at the outlet condenser and trap.

*Coghlan's degreasing plant* (Brit. Pat. 170,645—1921), shown in Fig. 120, has good points, and is suitable for ethylene trichloride. (1), (2), (3), and (4) are tanks, in which wire cages holding the wool are placed. These are connected by valves *a* to a vacuum pump at *e*. The solvent is contained in the

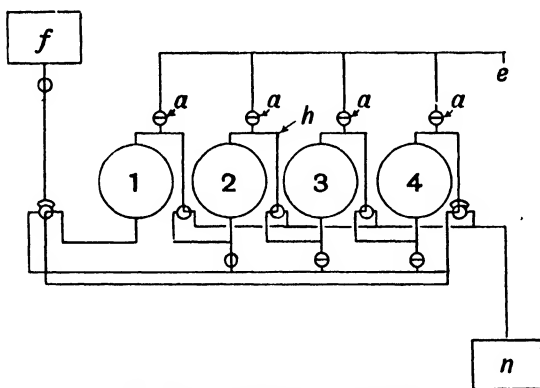


Fig. 120.—Coghlan's Apparatus.

reservoir *f*. From this it is run into tank (1) at a temperature of 45° C., and, after fifteen minutes, from tank (1) into tanks (2), (3), and (4) successively, and finally from tank (4) into the recovery tank *n*. Any tank may be filled with clean solvent from the reservoir *f*. After the extraction has been completed and the solvent has drained into the recovery tank *n*, that which remains in the wool is recovered by means of hot water or a stream of heated carbon dioxide. The contents of the tank *n* are then distilled to recover the grease and the solvent. The latter is returned to the reservoir *f*.

Although degreased wool is practically oil-free, it still contains the suint and some unremoved dirt. These impurities may be removed by washing it with warm water in a wool-washing machine. The suint itself contains sufficient soap to complete the removal of the dirt. The vegetable matter is then got rid of by carbonization. The recovered wool fat is used for the preparation of lanoline. The solution of suint, when evaporated to dryness and charred, gives rise to potassium carbonate. This is extracted from the charred mass with water.

**Scouring Raw Wool by the Emulsification Process.**—In spite of the advantages of the solvent process, wool is still generally scoured by means of soap and water, with or without the addition of an alkali carbonate. The operation is carried out in a washing machine. This consists essentially

of a long trough, provided with rakes, a false bottom, and at the exit a wringer.

The trough is filled with a soap solution maintained at a temperature of from 35° to 40° C. The wool is made to travel forward beneath the surface of the soap liquor in the trough, the liquor being kept in a state of gentle

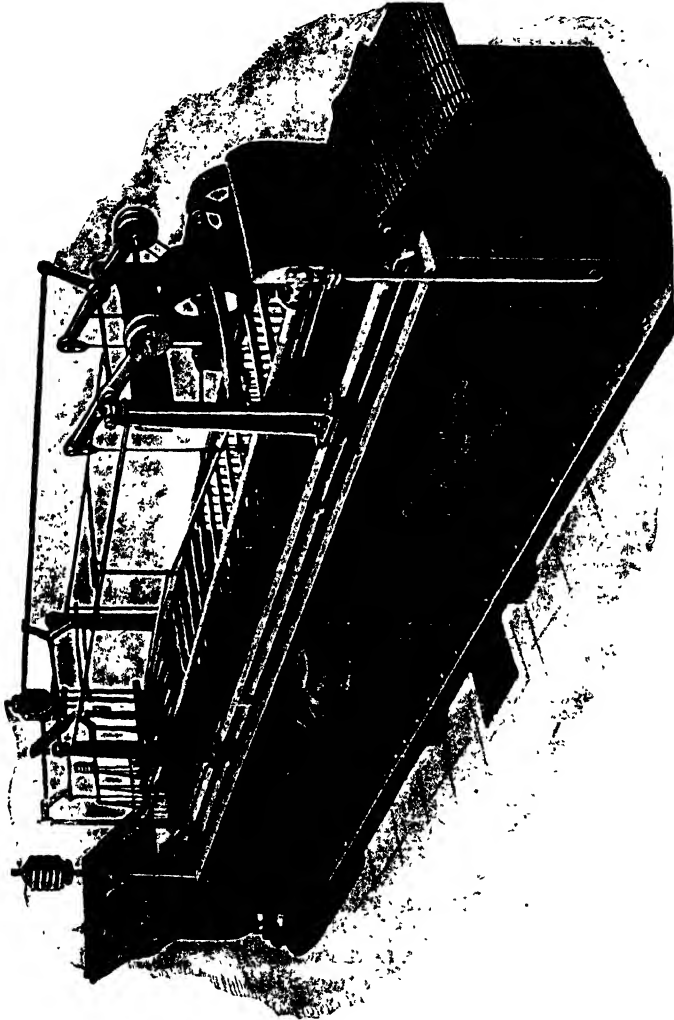


Fig. 121.—Charlesworth Wool-scouring Machine.

agitation to assist in emulsifying the oil and dirt. The latter either falls through the perforated bottom of the trough, or is carried in a state of colloidal solution in the soap liquor. As the wool leaves the trough, the excess of soap liquor is lightly squeezed out by the wringers. After this the wool may pass into another trough containing either fresh soap solution or water. The used soap liquors are collected for recovery of the oil and soap. The Charlesworth scouring machine is illustrated in Fig. 121.

The mechanical details vary in different types of apparatus. In the Dawson washing machine (Fig. 122—*J. Soc. Chem. Ind.*, 1905, 24, 435), in order to pass the wool continuously through the scouring tank, two series of rake frames *A* and *B* are employed, each approximately of the same length as the tank *A'*, and each composed of four or more longitudinal bars or tubes carrying prongs or forks *D*. Each bar or tube is provided, at the entrance end of the machine, with an immerser projecting downwards from it, and consisting of a narrow perforated chamber *F* of about the same width as the bar or tube. The bars or tubes have pivoted to them at each end, and at one or more intermediate points, arms *I*, attached at their tops to transverse bars *I'*, to each of which is connected a central rod *J*. The rods *J* may be coupled to one or more crank arms *J'*, or connected with the arms of a beam lever, with the object of causing the rake frames to rise and fall alternately, to be pushed

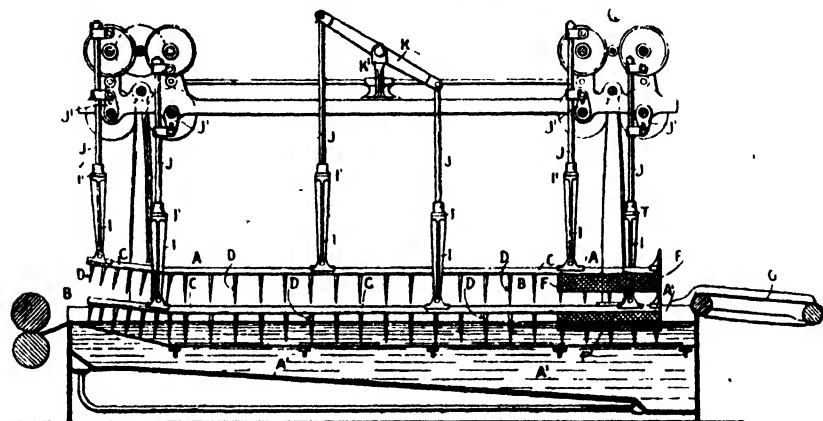


Fig. 122.—Dawson Scouring Machine.

forward when the prongs are to be immersed in the liquor contained in the tank, and to be carried backwards towards the entrance end of the machine when the prongs are out of the tank, prior to their entering the tank again.

A different type of washer is that of Bastin (*J. Soc. Chem. Ind.*, 1905, 24, 671). A cylinder *A* (Fig. 123), with openings *c* in it parallel to its axis, has within it a system of rakes or forks *B*, borne by frames *E* upon a number of shafts *F*, and which project outside the cylinder. An arm *G*, carrying a friction roller *d*, is mounted upon each of the shafts *F*. These rollers follow the curved guide-plates *H* and *K* outside the cylinder, their movement away from or nearer to the axis of the cylinder causing the forks to project out of or to enter the cylinder. The wool *L*, received in the washing or scouring tank, is seized by the forks, carried forward by them as they move with the cylinder, and then released at the point where the prongs of the forks are withdrawn into the cylinder.

In an alternative arrangement, fixed forks are employed. Portions of the surface of the cylinder are, in this case, constructed so as to be movable away from or towards the axis of the cylinder, their movement causing the forks to be either hidden or exposed, as the case may be.

In Walker's patent (*J. Soc. Chem. Ind.*, 1918, 37, 462A) the goods to be scoured are carried by a travelling apron under perforated cylinders, with or without vanes inside, and between groups of rollers situated between each

two cylinders throughout the length of a trough containing the scouring liquor. The material can be held on the apron by binding tapes or bands, which travel with the apron and return outside the trough above the cylinders. The action of the perforated cylinders is to cause the liquor to circulate in and out of the material in a vertical direction without disturbing its arrangement.

*The selection of a suitable soap is an important factor in wool-scouring. The soap used must be freely soluble in water at the temperature of the opera-*

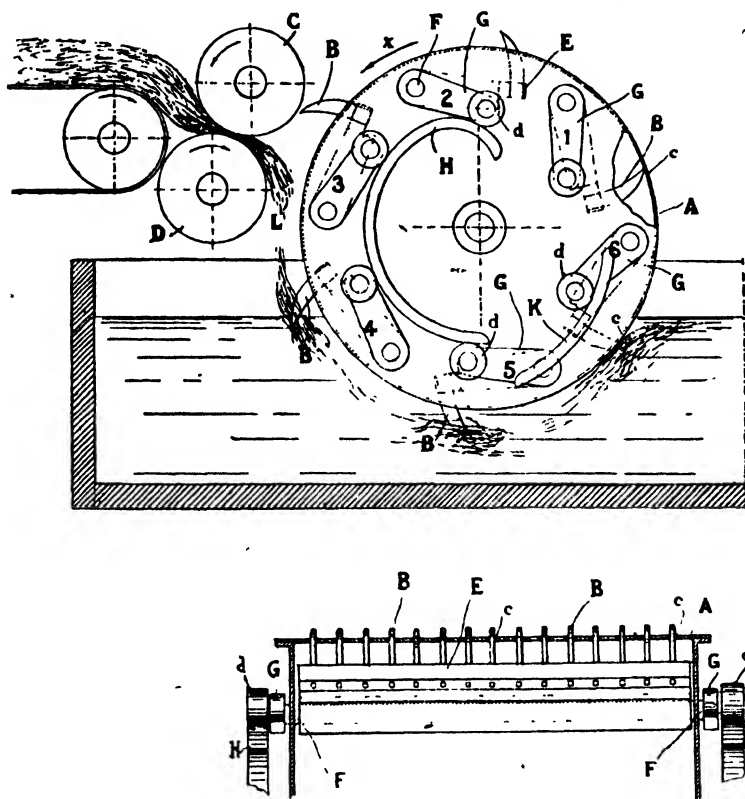


Fig. 123.—Bastin Wool Washer.

tion, and have, at the same time, a high emulsifying power. Potash olive-oil soap is, of course, the best, but free caustic alkali must be guarded against.

Mild alkali, such as ammonium or sodium carbonate, is very commonly used with soap. It increases the emulsifying power of a soap, but tends also to diminish the stability of the emulsion. Sodium carbonate is the cause of considerable damage to the fibre in wool-scouring, ammonium carbonate being less dangerous. Low-grade goods are sometimes scoured with sodium carbonate alone, its action being due to its power of saponifying the free fatty acids which are always present. Solutions of protective colloids, formaldehyde, sodium alginate, etc. are used to protect the wool against damage by alkali in scouring. According to Bennet's patent, protein degradation products (lysalbinic and protalbinic acids) make wool softer, more

elastic, and glossy, either if added to the scouring liquor or used afterwards. *E.g.* scour the yarn or cloth at 45° C. in a solution containing 15 parts of sodium carbonate, 5 of soap, and 45 of protein product. The latter is made by heating protein substances, such as casein, with 2 to 10 per cent. sodium-hydroxide solution for two to three hours at 80° to 85° C. After washing, the wool is dried, and, if necessary, carbonized.

During the processes of spinning, weaving, and knitting, oil or an emulsion of oil in soap and water is used to lubricate the fibres and render them supple. Olein, olive oil, neatsfoot oil, and sulphonated oils are all used. Unsaponifiable oil must be guarded against very carefully, since it is very difficult to remove afterwards by any emulsification process. Both oleins and neatsfoot oil not infrequently contain unsaponifiable oil, which is the cause of subsequent discoloration in white goods or light patches after dyeing. Yarns are also sometimes sized. The use of these oils makes it necessary to scour either the yarn or the pieces again before bleaching or dyeing. Soap and water, with or without sodium carbonate, are again employed. As a general rule, about 4 to 5 per cent. of soap and 2 to 3 per cent. of sodium carbonate are used, but ammonium carbonate is a safer form of alkali. The completeness of this scouring process depends upon the oils used in spinning and weaving and the presence or absence of calcium and magnesium soaps. The latter two cannot be removed, and mineral oil only very imperfectly. Yarns and piece-goods are often prepared for dyeing by washing with a solution of sodium carbonate alone. Thus yarns or pieces may be cleansed by washing in warm water containing from 1 to 3 lb. of sodium carbonate for each 100 lb.

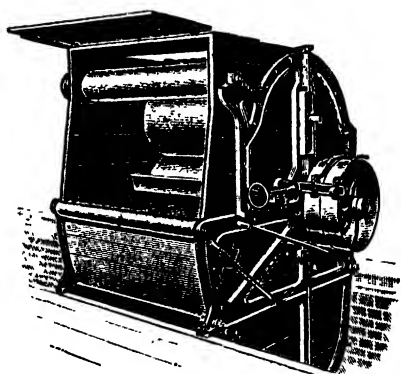


Fig. 124.—Whiteley's Scouring Machine.

of wool. In the case of loose wool, from 3 to 4 lb. of alkali is used for clean samples, while for greasy wool the amount may rise to about 10 lb. The use of much alkali is, however, always to be deprecated.

Pieces, or knitted tubular goods, can be joined end to end and treated in the open width, being passed through the scouring liquor by means of pairs of rollers. They are washed in the same manner. Or, alternatively, they are passed between rollers in the form of a rope, *i.e.* not in open width, and thus through the soap liquor. Whiteley's scouring machine is seen in Fig. 124.

The rope passes through the rollers, the lower one of which dips into the soap liquor in the trough beneath, and thus conveys it to the cloth. From there the rope passes over guide rollers into the liquor at the bottom of the machine. From this it goes again through the rollers, bringing soap liquor with it, which is squeezed out into the upper trough, from which it overflows or passes through holes into the lower part of the machine. When the scouring is complete, the soap liquor is run out, and the goods are washed with water in the same machine.

Scouring in open width is carried out in the same way. The only difference is that the goods pass between the rollers at their full width, and may also pass beneath a roller in the soap box to keep them in this condition. Hanks may be hung on sticks placed across the top of a vessel containing the soap solution, and turned occasionally to ensure equality of action. They are some-

times worked carefully by hand. After scouring, they are passed through a pair of carefully adjusted rollers, which squeeze the soap solution back into the bath, after which they are washed with warm water and hydro-extracted. Hank-washing machines are also employed. One made by Messrs. J. M.

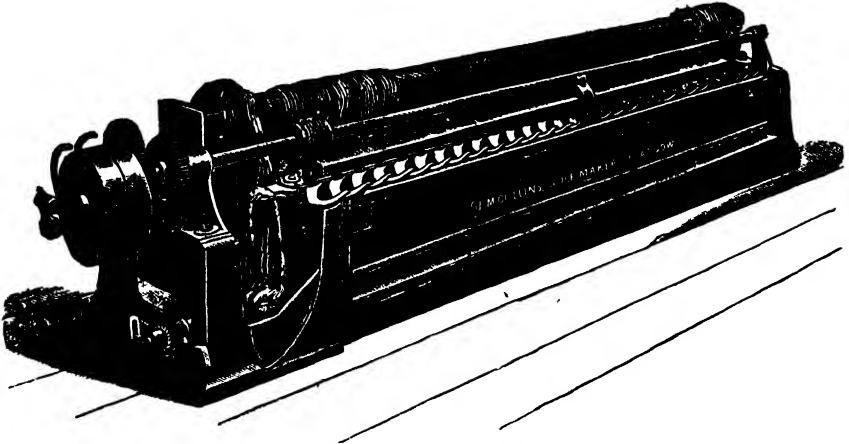


Fig. 125.--Hank-washing Machine.

Collins is illustrated in Fig. 125. In this the hanks are threaded on to the roller, and, after traversing the length of the machine, removed at the other end. Garments are sometimes joined together and treated in the rope form,

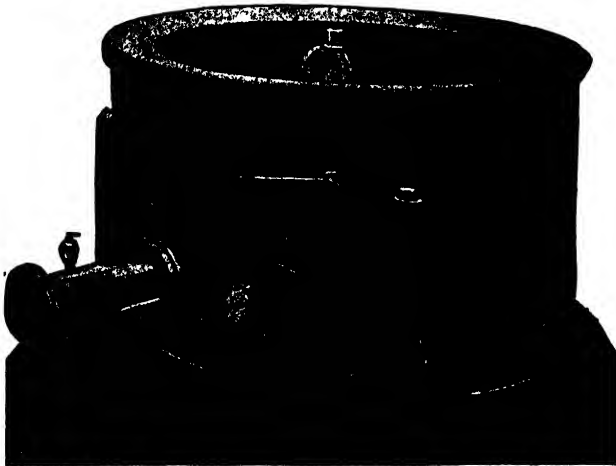


Fig. 126.—Steam-driven Centrifugal Hydro-extractor.

but more commonly they are washed in a dolly. When knitted goods are scoured, a certain amount of milling is introduced purposely to give the required handle; this is controlled by visual inspection from time to time.

*The Hydro-extractor.*—A convenient form of centrifuge is made by Messrs. Manlove & Alliott, and is illustrated in Fig. 126. The essential parts of a



hydro-extractor are a cage or basket made of some perforated material, connected to a vertical shaft, which gives it a rapid spinning motion about a vertical axis. The goods are thrown against the side of the basket, the water passing through the perforations into the outer case, and leaving by the outlet pipe.

For piece-goods such as tubular fabrics, capable of being dealt with in rope form, squeezing machines are frequently more convenient than centrifuges. Fig. 127 shows Cooke's roller squeezing machine, which works continuously and extracts 90 per cent. of the water present. It takes three ropes simultaneously.

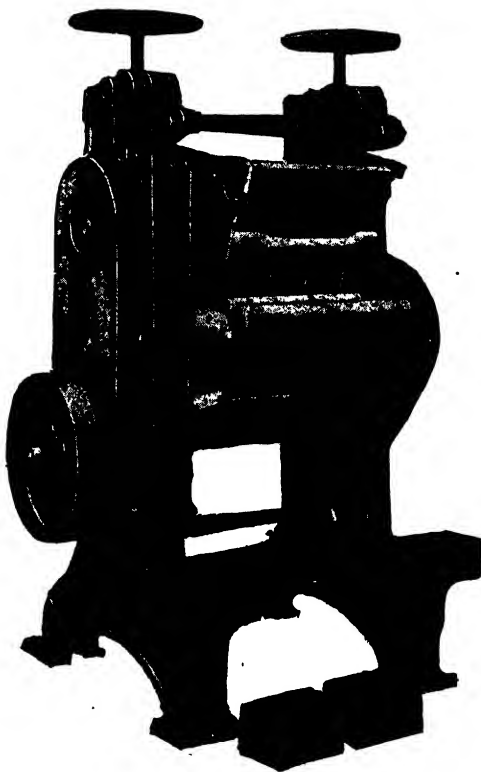


Fig. 127.—Cooke's Roller Squeezer.

**Removal of Oil.**—The scouring of knitted goods containing oil is often difficult. Speakman and Chamberlain (*Nature*, 1932, 130, 274) recommended the use of oleyl alcohol,  $C_{17}H_{33}.CH_2.OH$ , as an assistant, particularly when mineral oil is present. From 6 to 10 per cent. of the alcohol is required. Trotman and Horner (*J. Soc. Dyers Col.*, 1932, 48, 325) made extensive experiments on the scouring of knitted goods containing oil. They found that (i) sodium silicate is the most efficient assistant; (ii) no normal scouring process can be relied on to remove more than 96 per cent. of the total oil present; (iii) mineral oil is more difficult to remove than saponifiable oil—this is due partly to the surface tension between the oil and water; (iv) the presence of a small proportion of saponifiable oil assists the emulsification of

mineral oil and hence its removal; (v) the type of fabric affects the results—loosely-knitted crossbred web is easier to scour than tightly-knitted webs or Botany goods; (vi) increasing the viscosity of the scouring liquor assists the removal of mineral oil—the viscosity can be increased by means of sodium silicate, gum-tragacanth, agar-agar, etc.; (vii) olive-oil soap removes mineral oil better than a soap with a higher titer; (viii) increasing the volume of the bath does not affect the result; and (ix) whilst a second or third scour removes further portions of oil, some residual oil always remains, owing to back absorption taking place until an equilibrium is established. It may be noted that when mineral oil is absent, the use of a soap having a titer of 35° C. in the presence of sodium silicate gave the best results.

**Removal of Calcium and Magnesium Soaps.**—Woollen goods are sometimes contaminated with insoluble calcium and magnesium soaps. These cannot be removed by the ordinary scouring process. The goods must be soaked in a

dilute (about 1 per cent.) solution of hydrochloric acid. This decomposes the soaps, forming soluble calcium or magnesium chloride and free fatty acids. The goods are then washed with soft water to remove these chlorides, and the fatty acids are converted into soluble soaps by treatment with a dilute solution of sodium carbonate or ammonia. Iron is removed by treatment with acid and washing. Oxalic acid or its acid salts are good solvents for iron. Calgon,  $\text{Na}_2(\text{Na}_4\text{P}_6\text{O}_{18})$ , is useful for the removal of calcium and magnesium soaps. It may be added either to the scouring liquor or to the wash water. The compound sodium hexametaphosphate,  $\text{Na}_2(\text{Ca}_2\text{P}_6\text{O}_{18})$ , which is formed by interaction with soap, is soluble in water.

**Recovery of Waste Products.**—In the scouring of raw wool the soap liquors are run into large tanks, where much of the dirt settles to the bottom. The liquor is then thoroughly mixed with a slight excess of sulphuric acid. This decomposes the soap, liberating the fatty acids. These rise to the surface, and, if the mixing has been efficient, bring up all the grease with them, which was previously held in suspension or emulsion by the soap solution. The acid liquor is drawn off, and the crude magma of fatty acids and grease is allowed to drain as dry as possible. It is then packed in canvas bags, and pressed in a steam-heated filter-press. In this way a large proportion of the fat and fatty acids is pressed out and collected, and the residue in the press is extracted with benzene or other solvent to recover the remainder. The recovered grease is used for lubricating the wool during spinning, for the manufacture of lanoline, and even for making soap. It has a somewhat variable composition, being a mixture of wool-wax, fatty acids from the soap used in scouring, and the cholesterol and iso-cholesterol which were present in the free state in the wool. Lewkowitsch gives the following analysis of an average sample:—

	Per cent.
Volatile acids . . . . .	1.28
Insoluble free fatty acids . . . . .	20.22
Combined fatty acids . . . . .	48.47
Alcohols (cholesterol) . . . . .	36.47

Recovered grease is often distilled with superheated steam, the products being known as *distilled grease*. One product of distillation is *oleine*, which is used both for lubricating wool during spinning, and also for making oleine soaps. To prepare oleine, the distillate, which sets to a solid on cooling, is pressed, in order to remove the liquid fatty acids. These consist chiefly of oleic acid, and constitute oleine. The residue in the press gives recovered stearine.

The scouring liquors from the treatment of piece-goods are treated in the same way, and give a much cleaner product, containing but little wool-wax or cholesterol. The fatty acids obtained from these liquors can be converted into soap and used again.

Sometimes the liquors are precipitated by means of an iron salt, such as ferrous sulphate (copperas). In this case the precipitated iron soaps and entangled grease are collected, and decomposed with sulphuric acid. The iron is thus recovered as sulphate, and can be used again.

**Analysis of Scoured Wool.**—The efficiency of a scouring process may be judged by (i) the amount of unremoved oil in the fabric; (ii) the residual soap; (iii) the presence of calcium and magnesium soaps; and (iv) the proportion of damaged fibres. The analysis may be carried out in the following way:—

About 5 g. of the sample is dried in an oven, weighed in a stoppered weighing-bottle, and extracted in a Soxhlet extractor with ether or petroleum spirit to

remove the oil. After evaporating off the solvent, the residual fat in the flask is dried and weighed. The fat-free residual wool is then extracted with hot alcohol to dissolve out the sodium or potassium soaps. For this a continuous hot-chamber extractor, such as that illustrated in Fig. 118, is better than a Soxhlet. After extracting for about three hours, the alcoholic solution is filtered, if necessary, and the alcohol evaporated on a water-bath. The residue is dried and weighed. This may contain other bodies besides soap. To estimate the latter, the residue is dissolved in hot distilled water, and a measured volume, say 50 ml., of decinormal acid is added to decompose the soap and liberate the fatty acids. After boiling for a few minutes, the mixture is transferred to a separating-funnel, the beaker being washed out two or three times with small quantities of hot water. About 25 ml. of ether is poured into the beaker to dissolve any unremoved fatty acids, and, after gentle rotation, poured from the beaker into the funnel. The stopper of the separator is then replaced, and the contents are well shaken to dissolve the fatty acids. The lower layer is then carefully drawn off into a beaker, and the ether washed with about 10 ml. of water, this also being added to the contents of the beaker. The ethereal solution of the fatty acids is now poured into a weighed flask. The ether is evaporated, and the residual fatty acids are dried and weighed. If the weight of these is multiplied by 0.97, the result gives fatty anhydrides. The acid liquor in the beaker is now titrated with decinormal alkali, using methyl orange as indicator, to determine the amount of unused acid. Each millilitre of decinormal acid used in decomposing the soap corresponds to 0.0031 g. of sodium oxide,  $\text{Na}_2\text{O}$ . The sum of the sodium oxide and fatty anhydrides gives the soap present in the weight of fabric taken. Calcium and magnesium soaps, if present, will still remain in the fabric, being insoluble in both ether and alcohol. The fabric is soaked for about an hour in a dilute solution of hydrochloric acid (from 1 to 5 per cent.). This decomposes the insoluble soaps, free fatty acids and calcium or magnesium chloride being formed. The free fatty acids adhere to the fabric, and the excess of acid and the chlorides of calcium and magnesium are removed by washing with cold distilled water. The washed fabric is dried, and extracted with ether or petroleum spirit in a Soxhlet. After evaporating off the solvent, the fatty acids derived from calcium and magnesium soaps are left in the flask, and are dried and weighed.

Damaged fibres are identified by microscopic examination and counting the proportion present in 50 or 100 fibres.

**Oils used for Lubricating Wool.**—Any oil used should be capable of being removed easily by the scouring process. This means that it should be readily emulsifiable by soap. No oil emulsifies so easily as olive oil. In any case the more readily the oil can be saponified the better will it emulsify. Neatsfoot oil, if free from "foots," also emulsifies fairly readily. These two oils are used largely in the oiling of wool for spinning and in the preparation of emulsions for yarn used for knitting, etc. Mineral oil does not form good emulsions with soap and water, and is, therefore, very difficult to remove from goods by the scouring process. It can be completely removed only by an organic solvent (above). Hence, absence of unsaponifiable oil is very important. The determination of unsaponifiable matter is one of the most important tests for a wool oil. The presence of drying or rancid oils and rosin should also be guarded against, since both are difficult to remove in scouring, and if left in the goods cause stickiness and discolorations. Also, drying oils absorb oxygen, and during this process heat is developed which may be sufficient to cause spontaneous combustion. The oil should not have a low flash-point. In fact, the two

most important tests are (i) the percentage of unsaponifiable matter, and (ii) the flash-point, which should not be below  $170^{\circ}\text{C}$ .

**Determination of Flash-point.**—In the case of wool oils the *open test* is employed. About 50 ml. of the oil is placed in a nickel or porcelain dish of about 75 ml. capacity. The dish is then embedded in sand on a sand-bath, so that the sand is a little above the level of the oil. The bulb of a thermometer is placed in the oil, and the temperature raised slowly by heating the sand-bath with a small Bunsen flame. As the temperature rises, a second Bunsen flame is flashed on to the surface of the oil, till a slight flash of burning vapour is observed as the flame touches the oil. The temperature at which this takes place is known as the *flash-point*. The test should be repeated with a fresh quantity of oil, and the mean result taken.

Mackey's cloth-tester is used for testing liability to *spontaneous combustion* of fabrics when impregnated with the oil to be used for purposes of lubrication, etc. The following description of the apparatus (Fig. 128) is given in Allen's *Commercial Organic Analysis*, 1924, 2, 759. The apparatus consists of a cylindrical metal water-bath, the outside diameter of which is 6 in. and the inside diameter 4 in. The height of the bath is 7 in. outside and 4 in. inside, the depth of water inside with the lid on  $6\frac{1}{4}$  in. The lid is packed with asbestos wool and the tubes *A* and *B* serve to maintain a current of air. The cylinder *C* is made of wire gauze of 24 mesh per inch. The water-bath is open to the air and contains a ball of cotton-wool, oiled with the sample under examination. To perform the test, weigh out 14 g. of the sample into a shallow dish containing 7 g. of pure cotton-wool. Tease this out carefully by hand, so that the oil is distributed thoroughly throughout the mass: the success of the experiment depends upon the even distribution of the oil. Place the oiled cotton in the cage *C*, holding the thermometer

in its place while the cotton is being packed round it. Then bring the water in the jacket to vigorous boiling, place the cage in the air-bath, slip the lid down over the stem of the thermometer, and fix it in its place by means of the clamp *D*. Keep the water in the bath boiling, and note the temperature after the lapse of an hour. If the thermometer registers over  $100^{\circ}\text{C}$ . at the end of the first hour the oil must be regarded as dangerous. In the case of very dangerous oils the temperature may rise to  $200^{\circ}\text{C}$ . in an hour and a half. If it rises very rapidly to  $150^{\circ}\text{C}$ . it is best to withdraw the thermometer, as the cotton may ignite. It is important that no moisture should enter the air-bath.

Rosin may be detected in the soap solution obtained in the estimation of the unsaponifiable matter. This is returned to the separating-funnel and made acid with hydrochloric acid, and the mixed fatty acids are dissolved out with ether. The ethereal solution is separated and evaporated, and the test is applied to a little of the residual fatty acids as described for soap.

Emulsions of oil with sulphonated oils or their soaps are also used for oiling

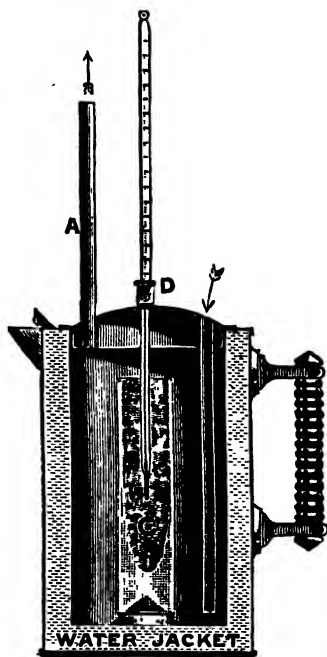


Fig. 128.—Mackey's Cloth-tester.

wool. Proprietary mixtures often consist of these together with a dissolved protective colloid such as hydrolysed glue. The name *soluble oil* is applied sometimes to a mixture of castor oil and alkali. Other mixtures contain sulphonated oils or oleates dissolved in organic solvents in the presence of free fatty acids. These preparations are in many cases protected by patents.

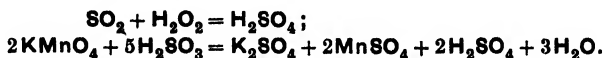
### The Bleaching of Wool.

The residual colouring-matters in scoured wool depend upon the variety of wool and the thoroughness with which the preliminary scouring has been done. Many types require little or no bleaching before dyeing. For white goods, wool is frequently simply tinted or "dyed white." For this process, 0.005 per cent. of methyl violet, acid violet, or alkali violet is used in a warm bath. With acid violet the bath should be made faintly acid with an organic acid; with the others a little soap may be used if desired. The goods are worked in the dye solution for about fifteen minutes at a temperature of 100° F. (37.8° C.), and then rinsed and dried. Tinted whites are not fast to washing or prolonged exposure to light.

Wool is generally bleached with sulphur dioxide, sulphurous acid, or hydrogen peroxide, the methods being very similar to those described for silk.

**Sulphur Dioxide.**—For sulphur dioxide the stove is used, from 5 to 7 lb. of sulphur being burnt for 100 lb. of wool. The damp goods are left exposed to the gas overnight. A considerable quantity of sulphur dioxide is adsorbed over and above that actually required to bleach the colouring-matters. The remainder is removed next morning by blowing out the chamber with air. The goods are then dried, either at once or after washing. It is very difficult to wash away all the sulphur dioxide with water alone. If acid-free goods are required for dyeing, a bath of dilute sodium carbonate is necessary, followed by further washing with water. Wool bleached with sulphur, like silk, gradually regains its colour on exposure to air. This change is hastened by washing or the action of alkalis. It is thought that perhaps the colouring-matters form oxidizable leuco compounds. Another theory is that a colourless but unstable compound of the colouring-matter with sulphurous acid is formed. Sulphur dioxide is often left in the bleached wool purposely to delay the reappearance of the colouring-matter. But bleached wool is also tinted in the same way as silk. The complete removal of residual sulphur dioxide from bleached wool is difficult, though it is necessary before dyeing, since if it is not removed the wool has an increased affinity for acid dyes, and in some cases may form leuco compounds with the dyestuff.

Sulphur dioxide may be converted into sulphuric acid by working the goods in a dilute solution of hydrogen peroxide, or by soaking in water and adding carefully a very dilute solution of potassium permanganate until a faint pink colour is produced, when they are immediately removed and washed. The removal of sulphur dioxide by the latter method is rather difficult, for if too much of the reagent is used, a brown deposit of oxide of manganese may be formed on the wool. If this happens, the goods should be put into a faintly acid bath containing a little peroxide. The removal of sulphur dioxide by these means is illustrated by the equations:

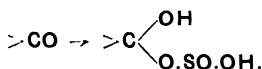


It will be noted that the treatment must be followed by an alkaline bath if acid-free goods are required.

Liquefied sulphur dioxide may be employed, but the white produced is not so good as when the gas is made by burning sulphur.

*Sodium bisulphite*,  $\text{NaHSO}_3$ , is used in the same way as for silk. About 10 per cent. on the weight of the goods is required. The white given by this process also is inferior to that produced by stoving.

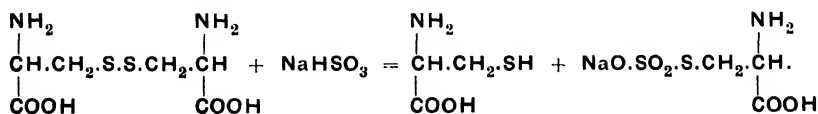
Raynes (*J. Text. Inst.*, 1926, **17**, T 379) found that at least two distinct components of wool combine with sulphur dioxide. One of these in nearly dry wool gives a pale yellow, unstable product in the presence of a high concentration of sulphur dioxide. The second combines with sulphur dioxide only in the presence of water, and may be a coloured carbonyl compound which gives a colourless addition product with sulphurous acid, thus:



This decomposes slowly in the presence of light and air or when washed with water, and alkalis accelerate the decomposition. The best results are obtained by using as high a concentration of sulphur dioxide as possible.

King (*J. Soc. Dyers Col.*, 1928, **44**, 14) found that azo dyestuffs react with sulphur dioxide in the presence of alkali to form azo-sulphites, which are lighter in colour than the dyestuff. He suggested that the colouring-matters of wool react in a similar manner, and could be bleached by solutions of sulphites similar in composition to those which effectively bleach azo dyestuffs. Experiments confirmed this conclusion, and the ratio of sulphur dioxide to sodium hydroxide most suitable for bleaching wool was found to be 1.0 : 1.25 to 1.0 : 1.35. The pH of such solutions is 6.8, and since they would be neutral to wool the process was referred to as *neutral bleaching*.

Phillips (*J. Soc. Dyers Col.*, 1938, **54**, 505) holds that the disulphide groups react with sodium sulphite, and that thiol and cysteine-S-sulphonate groups are produced in the wool. Sodium cysteine-S-sulphonate is obtained from cystine in accordance with the equation:



It is evident that the disulphide linkings of wool react with sulphur dioxide and sulphites in the same way as cystine.

**Bleaching with Peroxide.**—Hydrogen peroxide or sodium peroxide is used for the higher classes of goods or when a durable white is required. Unions of wool and cotton can be bleached, also, by peroxides without danger of tendering the cotton. Whites produced by peroxides do not require tinting. The methods used are practically the same as those described for silk, except that wool requires rather more bleaching. The bath is made up with about 15 gallons of ten- to twelve-volume peroxide diluted to 100 gallons with water. This gives an approximately 0.5 per cent. solution of peroxide. It is then made faintly alkaline with ammonia or sodium metasilicate, and about half a pound of soap or turkey-red oil for each 20 gallons of liquor may be added. As in the case of silk, excess of alkali must be avoided, and phenol red should be used as the indicator. The authors (*J. Soc. Dyers Col.*, 1926, **42**, 142) have shown that the best whites are obtained when the pH of the bath is the highest which

will not cause undue loss of weight or structural damage. The following results refer to wool: (i) better colours are obtained with sodium silicate than with ammonia for the same value of  $pH$ ; (ii) when using ammonia there is no increase in loss of weight between  $pH$  9 and 11; (iii) with sodium silicate the loss in weight is about the same at  $pH$  10 to 10.5 as at 9.0; at  $pH$  11 it begins to increase, and at  $pH$  12 is from 2 to 3 per cent. For most purposes a safe degree of alkalinity is that which changes the colour of phenol red but not that of phenolphthalein.

A two-volume standing bath is very suitable for wool. Weber (*J. Soc. Dyers Col.*, 1923, 39, 211) gives the following instructions: For a 240-gallon bath 200 gallons of water are heated up to  $130^{\circ}$  F. ( $54.4^{\circ}$  C.), the steam shut off, and 40 gallons of twelve-volume hydrogen peroxide added. Two pounds of sodium metasilicate dissolved in half a gallon of hot water are then stirred in. The goods are steeped in this bath for fifteen hours. After bleaching they are hydro-extracted, and the liquor is returned to the bath.

The liquor is then tested with permanganate, and made up to strength by the addition of more peroxide, the alkalinity being again adjusted, if necessary, with a little more sodium silicate.

As a rule the bleaching is started at a temperature of from  $100^{\circ}$  to  $120^{\circ}$  F. ( $37.8^{\circ}$ – $48.9^{\circ}$  C.). The goods, after wetting down, are entered, turned frequently during the first couple of hours, and then left overnight. Piece-goods are often bleached in a jigger, but in this case a stronger peroxide solution is required.

The necessity for good scouring and freedom from iron and dirt is even greater for wool than for silk.

Sodium metasilicate is preferable to ammonia for neutralizing the bath. Not only is the resulting solution more stable, but it undoubtedly gives a much better white.

Weber (*loc. cit.*) recommends the use of one pound of sodium metasilicate for each 20 gallons of ten- to twelve-volume peroxide. With this quantity the bath does not deteriorate rapidly in strength, and there is no danger of harshness in the goods, which is the case if larger quantities of sodium silicate are used. Iron, if present, is less likely to produce stains in a sodium-silicate than in an ammonia bath.

**Sodium-peroxide baths** are used in the same way as described for silk. The magnesium sulphate-peroxide bath is very useful for goods requiring much bleaching, but of course necessitates the use of an acid bath afterwards to dissolve any magnesium hydroxide which may be left on the goods. The peroxide bleach is sometimes combined with a subsequent treatment in a bisulphite bath or with stoving. After-treatment of goods bleached by peroxide with sodium hyposulphite has also been suggested. Thus Kershaw (Brit. Pat. 162,198—1920) soaks the goods in an alkaline peroxide bath for about sixteen hours, and then, after soaping, passes them through a cold bath of 8.5 per cent. sodium hyposulphite. Wool can be bleached with sodium hyposulphite alone, but the results are not better than those given by the cheaper sulphur dioxide.

The deleterious action of metallic catalysts and the effect of increasing  $pH$  of the bath have already been described. Goods which have been treated by the chlorination process for the production of an unshrinkable finish are often bleached with peroxide. In such cases it must be remembered that residual sulphurous acid will decompose its equivalent of hydrogen peroxide.

**Bleaching with Permanganate.**—Good whites can be obtained with this bleaching agent. About 0.6 or 1 per cent. is required. The wool is wetted

down in a bath of cold dilute sulphuric acid of about 1 per cent. strength. The permanganate solution is added either at once or at intervals during six hours. The goods are then rinsed, and passed into a bath of sulphurous acid or dilute hydrogen peroxide to reduce and dissolve the deposited oxides of manganese. After this they are washed thoroughly. If a solution of sulphuric acid of about 5° Tw. is used, the precipitation of oxides of manganese is prevented, and no reducing bath is required. While potassium permanganate gives good results if used carefully, excess must be avoided. Powerful oxidizing agents gradually oxidize the  $\text{NH}_2$ -groups, producing a yellowish tint which cannot be removed. This is more often seen when excess of sulphuric acid is used. The permanganate bleach is intermediate in cost between those of sulphur dioxide and hydrogen peroxide. It is particularly suitable for unions, in which the cotton would be tendered by stoving.

### The Finishing of Woollen Goods.

Woollen goods are, after bleaching, subjected to certain mechanical finishing processes to improve their lustre and general appearance, to regain width, and, in the case of garments, to impress a fixed shape upon them. Nearly all of these processes depend upon the property which wool has of becoming plastic when treated with hot water or steam. The finishing operations include the following:—

**Turning.**—Tubular fabrics are commonly turned inside out before treatment with scouring liquors, and also for certain mechanical finishing processes,



Fig. 129.—Widdowson's Turning Machine.

being finally re-turned before they are pressed. For this purpose a *turning machine* is used. One made by S. G. Widdowson & Co. is illustrated in Fig. 129. It consists of a hollow metal tube, 3 or 4 yards long, and 6 to 8 inches in diameter. One end is fixed, and at the other is fitted a ring carrying a number of polished metal revolving circular or cylindrical rollers. The fabric is drawn over the tube. A hook attached to a string is fastened to one end of the fabric. A small weight fastened to the other end of the string is then thrown through the tube, and by means of the string the fabric is drawn through from outside to inside, being, of course, turned during the process. It is then either rolled or folded as required by passing through a suitable apparatus. Widdowson's rolling and folding machine (Fig. 130) is easily combined with a turning machine. From the latter the fabric passes over an adjustable metal stretcher, through rollers which tend to impress upon it the recovered width, and generally straighten it out. It is then either wound on a roller or folded by passing over the top part of the frame, to which is imparted a regular swinging motion.

**Fulling or Milling.**—Fulling is the closing up of the fabric to give it more body and a soft feel. It is used chiefly for hosiery goods. This effect is produced, generally, during the scouring. The warm soap and water used



render the wool plastic, and as the fabric goes through the rollers the threads are pressed together, and a certain amount of shrinkage results, accompanied also by incipient felting. This gives the goods a fuller and softer feel. The

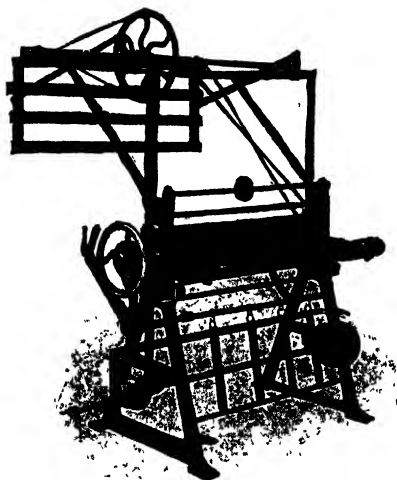


Fig. 130.—Widdowson's Rolling and Folding Machine.

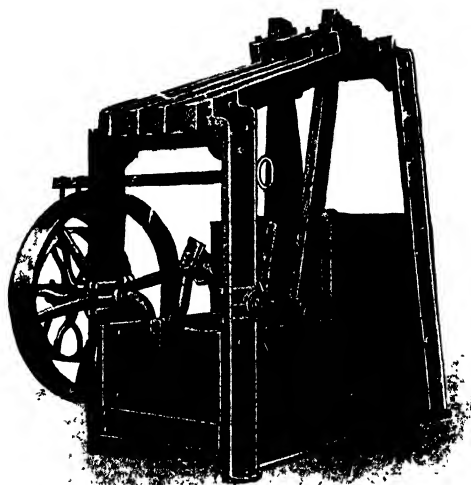


Fig. 131.—Pegg's Fulling Mill.

process must be stopped before actual felting takes place. Fulling may be applied also as a separate process. A fulling mill made by Messrs. S. Pegg & Son is illustrated in Fig. 131. In this the goods are placed in a warm

solution of soap in water, and subjected to the action of falling hammers or beaters. The same effect is produced by the dolly described for the soaping of cotton goods (p. 301).

If the fulling is carried too far, felting is produced. This is termed *milling*, and is thus only an extreme form of fulling. Milling is applied to cloth in order to close up completely the interstices between the weft threads and give

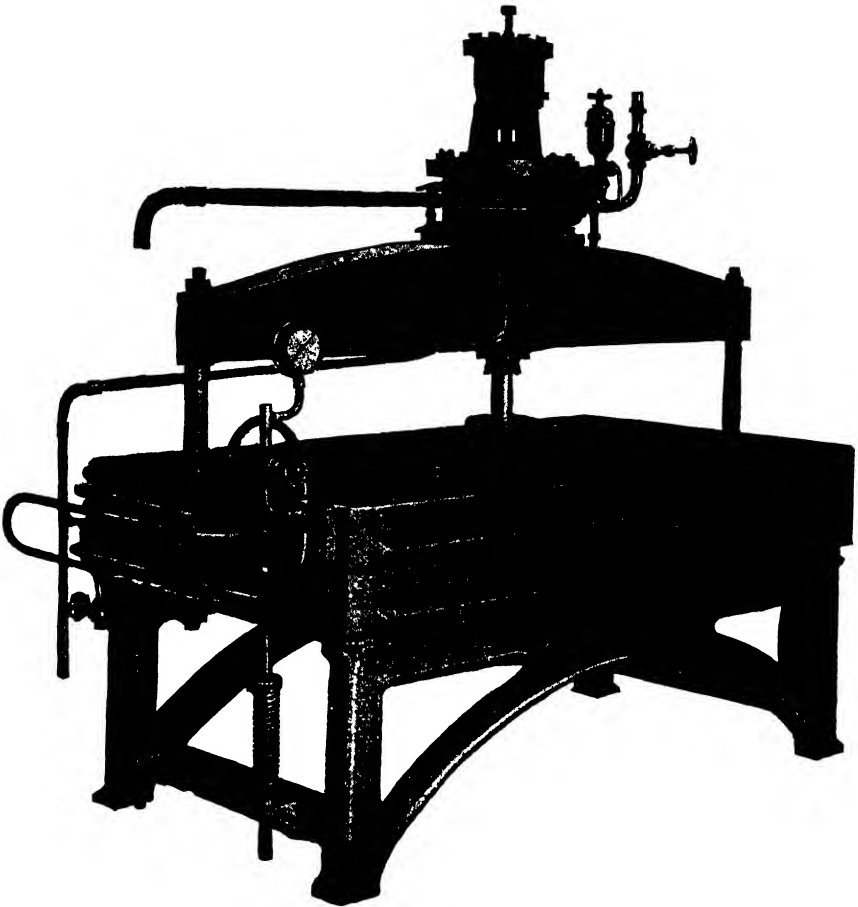


Fig. 132.—Steam-operated Press. (Gimson & Co., Ltd.)

solidity and firmness. In a milling machine the cloth passes continuously, in the rope form, first through a soap solution and then between rollers into a narrow spout, pressure being applied to the farther end of the upper side of the spout. This causes the cloth to become pressed together, thus producing felting. The operation is continued till a sufficient effect is produced.

**Pressing or Boarding.**—In this process piece-goods or garments are heated with steam in a press and allowed to cool under tension. Creases are smoothed out, lustre and handle are improved, and width is recovered. In the case of garments a permanent shape also is imparted to the goods. A steam-operated press is shown in Fig. 132. The bed of the press is raised or lowered by steam

or compressed air, the piston rod of a direct-acting steam cylinder being connected to the loose bed.

For the finishing of hosiery or tubular webbing, multiple-roller pressing (or calendering) machines are employed. These recover and maintain the desired width, and by varying the steam and roller pressures the type of finish can be controlled. A suitable machine is made by the Hunt Patent Hosiery Finishing Machine Co. The web may be put on dry. A steaming arrangement supplies the moisture required to give the finishing effect. After the web has left the stretcher the width is maintained constant throughout the operation, and the

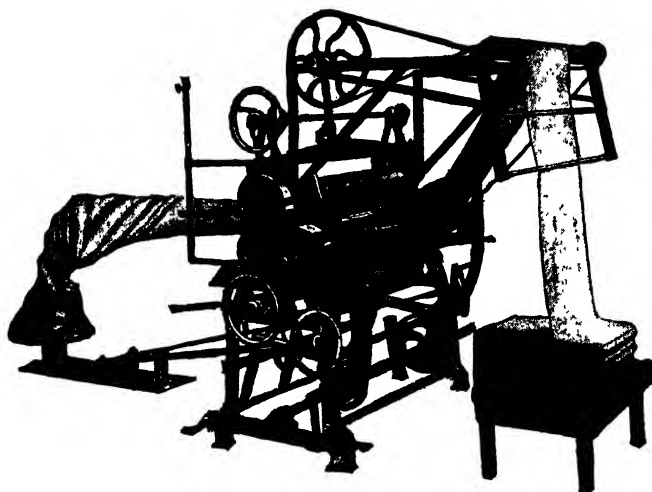


Fig. 133.—Widdowson's Hosiery-finishing Machine.

pressure may be varied to suit the material. A similar machine made by S. G. Widdowson & Co. is seen in Fig. 133.

**Nap-raising.**—When it is desired to raise the nap on a fabric, a rotating cylinder set with teazles or wire brushes is employed. A simple teazle brusher made by S. G. Widdowson & Co. is illustrated in Fig. 134, and a nap-raising machine in Fig. 135. Tomlinson's nap-raising machine (Fig. 136) is more complicated, and suitable for all kinds of fabrics.

**Crabbing.**—Some kinds of goods acquire a cockled appearance during manufacture. This is particularly observed with wool and cotton or wool and silk mixtures. *Crabbing* is the name applied to the process designed to smooth out the surface and remove the cockles. It consists in steaming and pressing, or in steaming or heating in boiling water and cooling under tension. The cockles are caused by the shrinking of the wool. Under the influence of steam or hot water the wool becomes plastic, and can be stretched to its original length. If the fabric is cooled in the stretched condition, the set becomes permanent. Yarns are crabbed by stretching the hanks on a frame, which is then immersed in boiling water, and finally cooling in the stretched condition by means of cold water. Piece-goods are passed through boiling water under both longitudinal and lateral tension, and wound on to cylinders in the stretched and plastic state. The plastic fibres are then caused to set by treatment with cold water.

**Decatizing.**—This is very similar to crabbing, except that steam is used

instead of boiling water. The cloth is wound on to a roller or cylinder, the surface of which is perforated with small holes through which steam can be

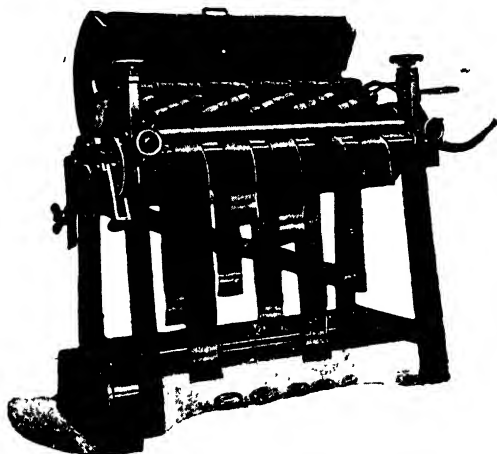


Fig. 134.—Teazle Wool-brusher.

admitted. The air is removed from the goods by means of a vacuum. Steam at a pressure of from 10 to 30 lb. is then admitted for about ten minutes, after which the goods are cooled by a current of cold air or water. They are then

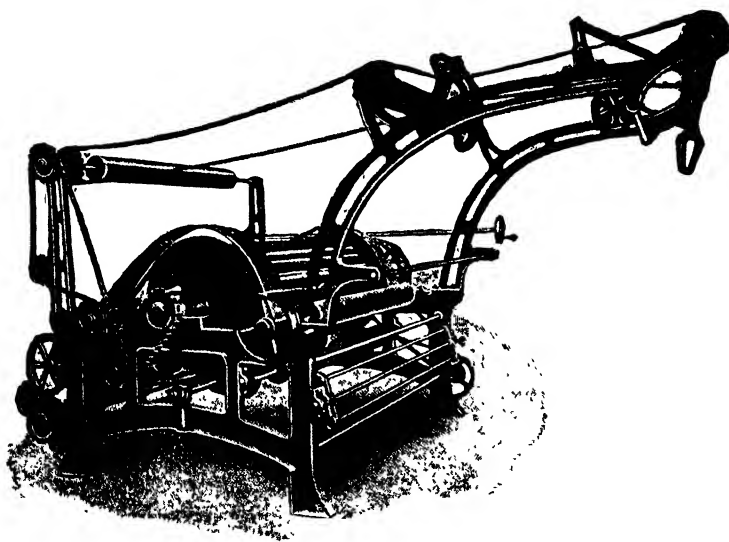


Fig. 135.—Widdowson's Nap-raising Machine.

wound on to a second cylinder, and the operation is repeated. After winding on to the second cylinder the position of the outer and inner ends of the cloth is reversed, thus ensuring equality of treatment. A more severe form of decatizing is termed **potting**. In this the cloth may be given a prolonged

treatment with steam, or boiled for several days with water, with the object of improving its texture and feel.

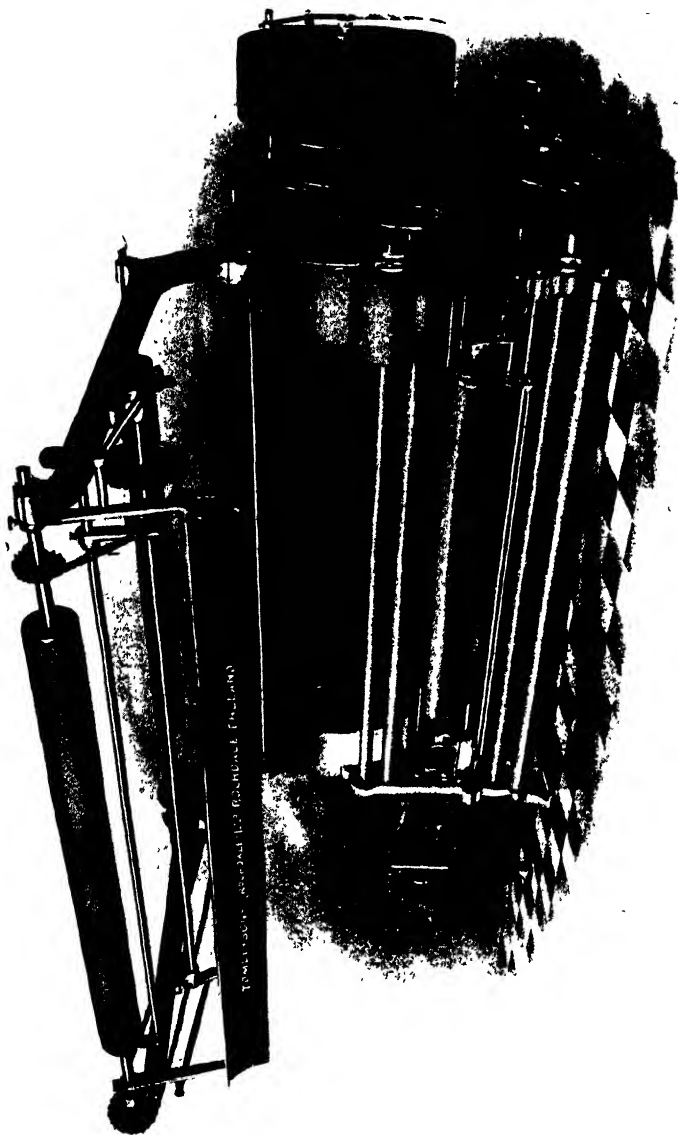


Fig. 136.—Nap-raising Machine.

All of these finishing processes may be applied to either dyed or undyed goods. If used for the former, the dyestuffs used must be sufficiently fast to stand the treatment. In the catalogues of dye-manufacturers details are generally given as to the degree of fastness of a dyestuff to these processes.

## CHAPTER XXII.

### THE SCOURING AND BLEACHING OF COTTON.

WHILE the dyer may have to scour and bleach both wool and silk, he is rarely required to bleach cotton. This needs complicated apparatus, and the operations are many and difficult; hence cotton-bleaching is carried out as a separate trade, and the dyer receives the goods either scoured or bleached as may be necessary. The preparation of cotton for dyeing is, however, part of his duty. Cotton goods are prepared for dyeing by boiling with water, either in open vessels or in closed keirs under low pressure, viz. from 2 to 10 lb. Of course, care must be taken, especially if open vessels are used, to see that the goods are kept below the surface of the water all the time. Closed pressure keirs are provided with some arrangement to ensure circulation of the liquor. After boiling for about three hours, the water is run off, and the goods are then washed with clean water and hydro-extracted. If the cotton appears to be dirty, from 1 to 2 per cent. of sodium carbonate with or without the same amount of soap may be added to the water. If sodium carbonate is used, the subsequent washing must be very thorough, since any residual alkali may cause trouble in the dye-bath.

Small lots of cotton may be bleached by any of the methods described later.

#### General Outline of the Process.

Since a knowledge of the processes employed by the cotton-bleacher is essential to a dyer, an outline of them will now be given. Further information may be obtained from S. R. Trotman and E. L. Thorp's *The Principles of Bleaching and Finishing of Cotton* (Griffin & Co.).

The impurities naturally present in cotton are: (i) cotton oil and wax; (ii) proteins and soluble amino compounds; (iii) pectoses, pectins, and pectates; (iv) natural colouring-matters; (v) impurities introduced during spinning or weaving, such as oil, size, or dirt. The bulk of the goods are treated in the piece form, though, of course, yarn and even loose cotton have to be dealt with. The details of the process depend upon the purpose for which the bleached goods are required. The pieces are stitched together end to end, and treated either in the form of a rope or at open width. The former is more convenient, and does not entail the use of such expensive plant as treating in open width. The rope is transmitted from process to process by means of washing machines, winces, and pot-eyes. The washing machine (Fig. 137) consists essentially of a pair of rollers, placed above a water-beck or box, provided with a mechanism for agitating the cloth while in contact with the water.

The goods are threaded and drawn through a series of glazed earthenware

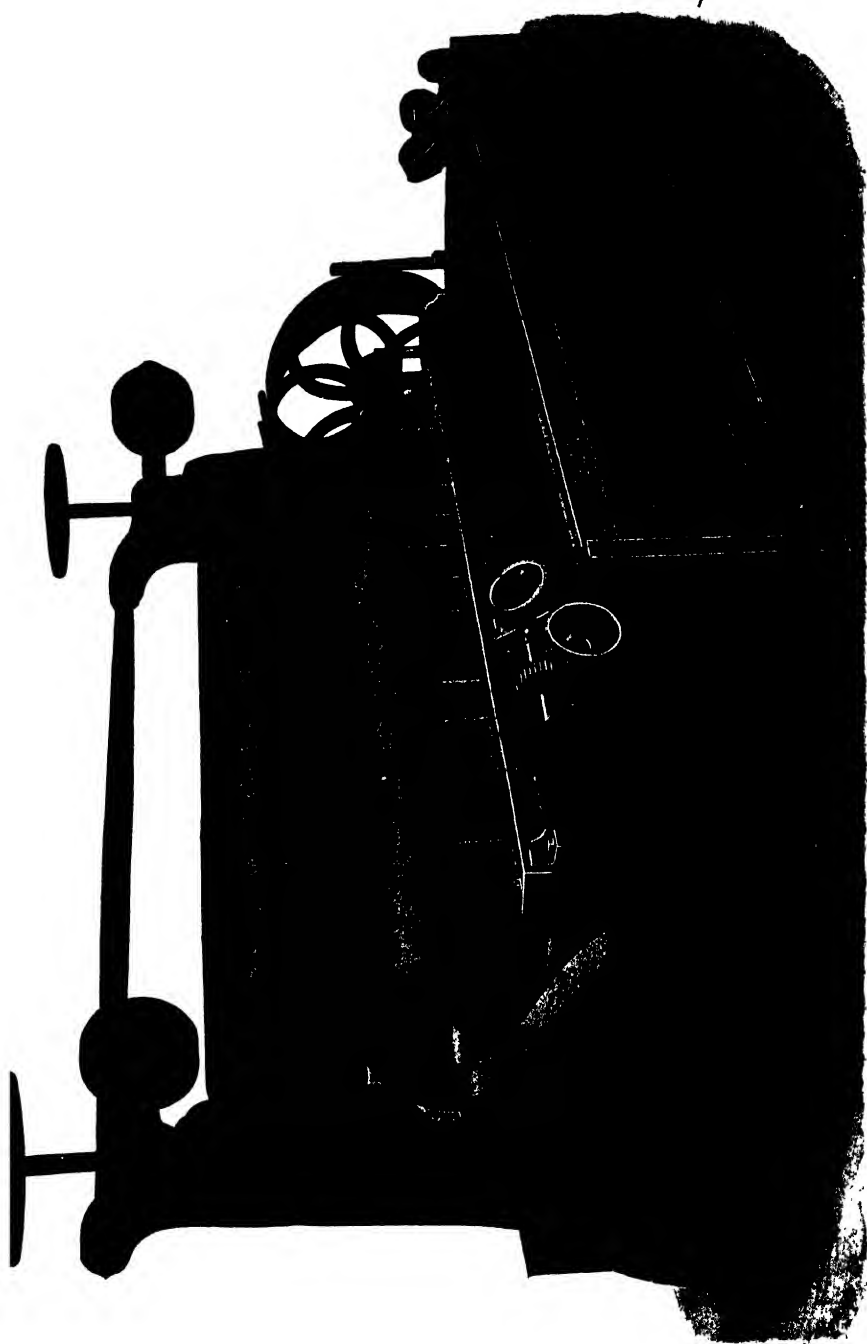


Fig. 137.—Roller Washing Machine.

rings, termed *pot-eyes* (Fig. 138), which direct their course to the next machine. Beyond the washing machine the passage of the cloth is guided by means of *winces* or drums (Fig. 139), which consist of six or eight wooden lags mounted on a shaft by means of rings carrying peripheral lugs, to which the lags are bolted. The peripheral speed of the revolving wince exceeds that of the washing machine by from 10 to 15 per cent., and the transmission of the cloth over these is brought about by the friction between it and the wince.

The driving shafts are controlled by friction clutches to allow of instant disengagement if necessary. The tension of the goods may be controlled by using more or fewer pot-eyes, or by placing them in such positions as to increase or diminish tension. It should be noted that if there is insufficient tension

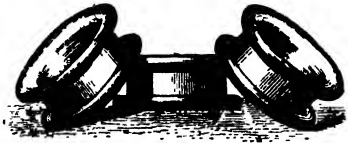


Fig. 138.—Pot-eyes

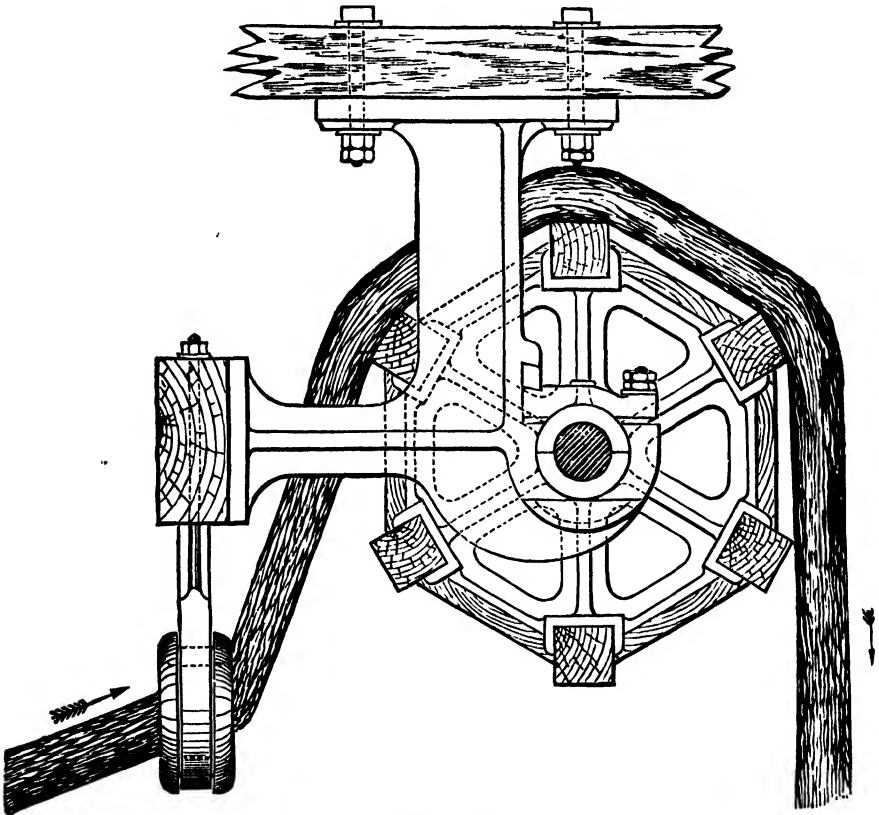


Fig. 139.—Wince.

there will be too great a loss in length after finishing the operations. On the other hand, too much tension may damage the goods.

The disadvantage of treating goods in the rope form is that no attempt is made to maintain their width or to prevent longitudinal distortion. One selvage is generally in front of the other, so that the weft threads lie diagonally



between the two. The selvages are subsequently adjusted and the threads straightened by the application of suitable tension or drag on the leading selvage, and width is recovered by stretching machines such as stenters.

Yarn in hanks also may be treated in the rope form by threading the hanks in the manner illustrated in Fig. 140, or by untying the bundles and



Fig. 140.—Chain of Hank Yarn.

reassembling them in a more open form, using one of the hanks as a binder, as shown in Fig. 141. In both of these forms the knots must be kept as loose as possible, and the bundles rearranged or the chain re-formed between successive processes in order to ensure complete penetration of the knotted portions. Small lots of hanks may be treated by twisting each lightly into a *noddle*

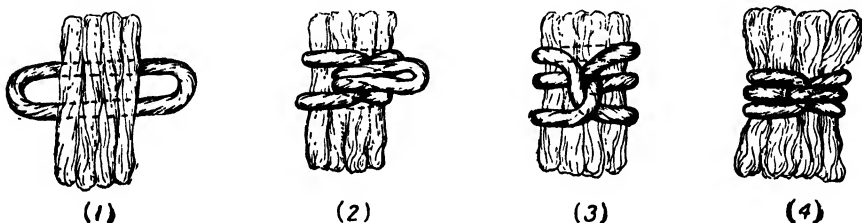


Fig. 141.—Yarn in Loose Bundles.

(Fig. 142). This enables them to be handled without danger of the threads becoming entangled, and they can be opened out again readily when required.

There are two general methods of working. Either the goods are stationary and the liquors moving, or, vice-versa, the goods move through stationary liquors. Sometimes, however, both goods and liquors are in motion together, as, for example, when goods are washed by passing them over a revolving wheel while they are subjected to a spray of water.



Fig. 142.—One hank bundle or *noddle* for isolating short hank yarn.

**Preliminary Operations.**—The unbleached or *grey* cloth is checked and examined upon receipt, and, if piece-goods, stamped with identification marks. The goods are then stitched end to end to form a “rope” or continuous piece.

**Singeing.**—Cloth is sometimes singed before being treated further. The object of this is to remove the nap. A singeing machine is used. It consists essentially of a copper plate slightly barrelled and of circular or U-shaped section, set in fireclay and forming the crown of a horizontal flue. The plate is heated by means of a coke or oil furnace, or by gas. The cloth is drawn over the heated plate in open width by the

rollers of a washing mangle. The speed at which it passes over the plate must be carefully adjusted so as to destroy the nap without burning the cloth. Sometimes cloth is singed by direct contact with a row of Bunsen burners. In this case it passes under a water-cooled roller, and the flames impinge on its under-surface during its momentary passage. Not only does

singeing remove the nap, but it also tends to break down and disintegrate any notes which may be present, and thus to facilitate their removal later. Sized goods containing such bodies as magnesium chloride are, however, liable to become tendered under the influence of the heat.

**Steeping.**—The first process of the bleaching operations is steeping, though it is not universally made use of. It consists in soaking the goods for some hours in water in order to soften and dissolve any impurities which are soluble. If the process is continued till natural fermentation sets in, the starch, present as size, will be changed into soluble dextrose or dextrin, and the cotton proteins also partly dissolved as peptones. Heavily sized goods are frequently treated with diastase in order to remove starch. The properties of this enzyme have been described already in Chapter IV. There are many commercial preparations of diastase, such as *diastafor*. About 1 per cent., on the weight of the goods, is dissolved in water, and either the cotton is soaked in this solution, at a temperature of about 65° C., or the goods are simply impregnated with the warm solution and piled for some hours. *Diastrol* is a similar preparation to diastase, but contains animal amylolytic enzymes. One part of it is said to be capable of liquefying 25,000 of starch. *Rapidas* (see Chapter IV) is suitable also, and can be used at a much higher temperature than diastase. Pancreatin also may be used as an assistant in steeping. It acts best in a faintly alkaline solution, and rapidly converts proteins into soluble bodies. Röhm has patented the method of digesting fabrics with a 0.1 per cent. solution of pancreatin, and claims that they are thereby completely freed from nitrogenous impurities.

When no starch has to be removed, the best preliminary treatment is to soak the goods in a solution of hydrochloric acid of about 0.5 per cent. concentration. This dissolves nearly all of the mineral impurities, besides opening the fibres and thus rendering them more amenable to the subsequent processes.

After the preliminary steeping, the goods are washed. It is very important in cotton-bleaching that the soluble products formed by one process should be completely removed before subjecting the goods to the next. The main principle underlying the whole process is that the insoluble impurities are, by means of a suitable chemical action, changed successively into soluble bodies, which can then be removed by means of water; and if they are not removed, they are, as a rule, re-precipitated by the next process, or inhibit the action of the chemicals used. Hence, between any two successive operations, thorough washing with water must be interposed. This is done by passing the goods through one or more machines similar to that shown in Fig. 137.

**Lye Boiling.**—This follows the preliminary processes described above. The lye boiling or *bowking* is the most important operation in cotton-bleaching. It is, in fact, the foundation of good bleaching. It consists, briefly, in boiling the goods with a dilute solution of an alkali to render soluble all the impurities other than certain natural colouring-matters, and thus enable them to be washed away with water. Oil, waxes, and mineral oils are saponified or emulsified; proteins are hydrolysed into soluble peptones or simpler amino compounds; pectoses and pectins are converted into soluble salts of pectic or metapectic acid; dirt is removed by gravity owing to the solution of the cementing grease; while most of the mineral matter is washed away with the lye. The boiling is carried out in specially constructed steel vessels known as *keirs*. They may be either open or loosely covered, in which case the liquor boils at the ordinary temperature, or closed like a "Papin's

digester," when the temperature corresponds with the steam pressure produced. The heating is carried out by steam pipes or direct steam, and some mechanical or automatic method of maintaining circulation is always provided, since the goods themselves are stationary. The effect of boiling under pressure, and thus raising the temperature, is to increase the rate at which saponification and hydrolysis proceed, thus shortening the time required to carry out the operation.

*Keirs.*—From a mechanical point of view the *injector keir* is the simplest, being readily adjusted for both high and low pressures; it may be taken, therefore, to illustrate the principles of construction. Fuller information

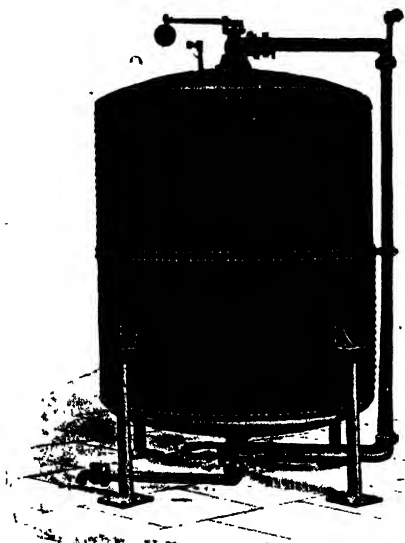


Fig. 143.—High-pressure Keir with External-injector Circulation.

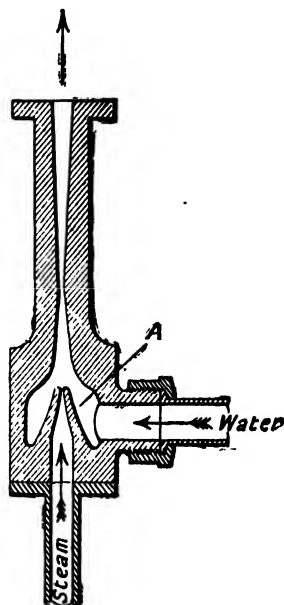


Fig. 144.—Injector.

about other types of keirs may be obtained from Trotman and Thorp, *op. cit.* The external appearance of an injector keir is shown in Fig. 143, which represents a keir made by Messrs. J. Walker & Sons, Ltd., while one is shown in section in Fig. 145. It consists of a cylindrical shell with dished ends, the lower of which is covered with an iron grid or false bottom. At the top are manholes for the entry of the goods. These are provided with covers placed in the inside and fastened by a bolt which passes through a saddle spanning the manhole externally. Circulation is maintained by an injector, which may be either outside the keir, or placed inside at the centre in the form known as a *puffer pipe*.

A simple form of injector is shown in Fig. 144. It consists of a water chamber *A*, with an orifice the shape of which resembles that of two hollow cones, one inverted above the other. Within the chamber, and placed concentrically with regard to the orifice, is a conical steam nozzle. The chamber and nozzle are fed by liquor and steam pipes. On issuing from the nozzle the steam meets the incoming liquor. This produces two results: (i) the

steam owing to its pressure emerges with a high velocity, communicating part of this velocity to the liquor; and (ii) at the same time the steam is condensed by the cooler liquor, so that a column of hot liquor emerges from the cone.

The puffer pipe (Fig. 145) consists of a conical base, fixed in the well of the keir, with apertures for the inlet of the liquor which has drained through

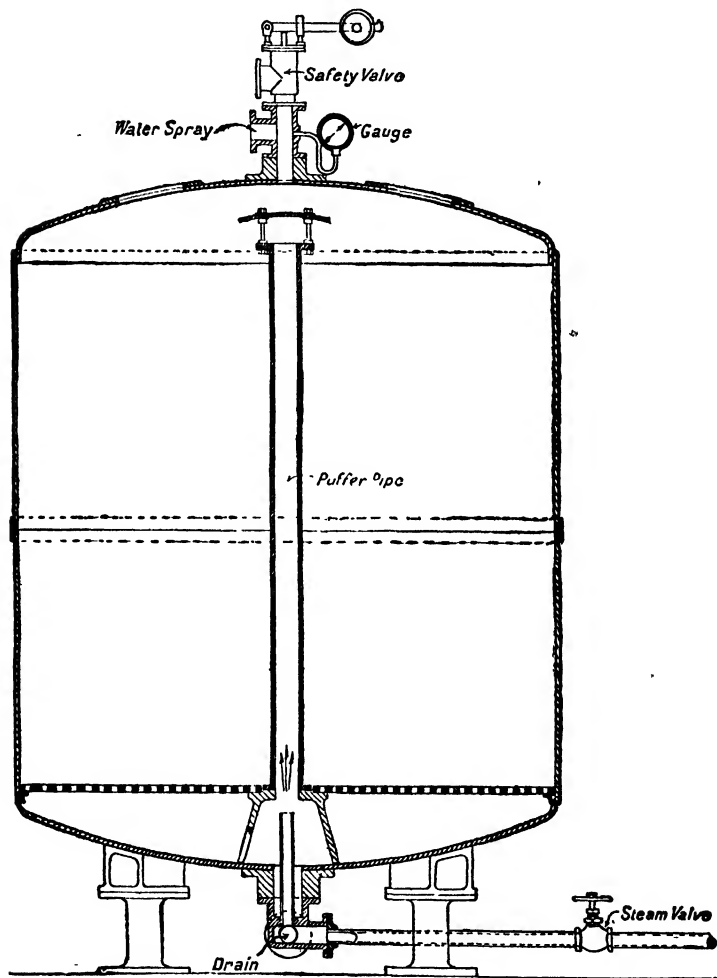


Fig. 145.—High-pressure Keir.

the cloth into the well. A vertical pipe of 4 to 5 inches bore is attached to the conical base, surmounted by a spreader or bonnet. A steam nozzle rises in the centre of the base, just below the vertical discharge pipe. The well liquor rises in the pipe to a height depending on the quantity in the keir. The steam from the nozzle, discharging into this column of liquor, heats and expands it till a point is reached when the steam ceases to be condensed, and ejects the column of liquor bodily from the discharge pipe against the bonnet,

from which it falls on to the goods. Meanwhile a fresh column of liquor rises in the pipe, and allows a subsidence of the goods. The hot liquor from the bonnet percolates through the goods back into the well, and the process is repeated. It should be noted that when the lye is heated directly with steam, progressive dilution occurs, which has to be allowed for in filling the keir.

Circulation is provided for in some keirs by a centrifugal pump or other device. In others the liquor is stationary, and the goods circulate through it.

**Methods of Lye Boiling.**—There are two methods of lye boiling: (i) the caustic-soda boil, and (ii) the lime boil. The former is simpler and less likely to cause mechanical damage to the goods. It is used largely for delicate goods, such as lace. The lime boil is employed chiefly for cotton cloth.

**The Caustic-soda Boil.**—The goods are impregnated with a dilute solution of caustic soda (about 2 per cent.), and packed in the keir. This process of packing is known as *plaiting*. It must be done in such a way that there are no hard places, the goods being distributed perfectly evenly. If the plaiting is uneven, regular circulation is impossible, since the liquors during their passage through the goods will always follow the lines of least resistance, thus leaving tightly packed portions unacted upon, and, therefore, incompletely treated. Plaiting is performed as follows: The cloth is fed into the keir in the rope form by means of an overhead wince, two ends being fed simultaneously, one to each half of the keir. As the cloth descends it is guided by the *plaiter*, by means of a short staff, into a series of laps, with which he forms a uniformly distributed layer conforming to the semicircular shape of his half of the keir. This is repeated in layers, with frequent changes in the direction of plaiting, so as to place laps in successive layers crosswise to each other. This prevents entangling, and makes the resistance of the cloth to the passage of the liquor uniform. The plaiter, who stands on the goods within the keir, shod with clean rubber boots or special clogs, meanwhile treads down the goods into a compact uniform mass. Sometimes the plaiting is performed by a mechanical contrivance. For example, the rope is fed through a tube something like an elephant's trunk, which by oscillating in a particular manner imparts a wavelike motion to it, causing it to form a series of folds.

After the goods have been packed in the keir, they are covered with the dilute solution of caustic soda. From 2 to 5 per cent. of sodium hydroxide on the weight of the fabric should be present. There is no need to have great excess, but there must be sufficient to complete the chemical reaction. The lid is then screwed down, and the heating commenced. The valves are, however, left open for a time after boiling has commenced to allow any dissolved air to be expelled. If oxygen is present in the keir there will be danger of oxycellulose being formed, accompanied by tenderness. The expulsion of air is assisted by letting the lye enter at the bottom of the keir, so that it displaces air imprisoned in the folds of the goods as it ascends. After the expulsion of the air, the valves are closed, and the keir is heated to a temperature of about 130° C. for several hours. The relation between pressure and temperature at which water boils is seen from Table XLIII.

When the boiling is complete, the lye is run off to a special tank, and the goods are washed in the keir, without opening it, with hot water. This process should be carried out in the absence of air, since the introduction of oxygen before the alkali is removed may produce oxycellulose. Moreover, if the keir is opened and the hot goods are exposed to the air, rapid evaporation of water

TABLE XLIII.—PRESSURE AND TEMPERATURE OF SATURATED STEAM.

Pressure, atmospheres.	Temperature of Steam, °C.
1.00	100.00° C.
1.25	106.33° C.
1.50	111.33° C.
1.75	116.50° C.
2.00	120.64° C.
2.25	124.39° C.
2.50	127.33° C.
2.75	130.98° C.

takes place at the exposed surface. This causes concentration of the alkaline liquor, which may cause incipient mercerization and shrinkage. Thorough washing is required, not only to remove the soluble products of the reaction, but also because cotton has the power of adsorbing sodium hydroxide, which it gives up only when repeatedly washed with hot water. The washing may be regarded as satisfactory when the goods no longer react with phenolphthalein. They are then ready for the next process. They should now contain only traces of nitrogen (which is a constituent of the colouring-matter), no proteins or other amino compounds, no pectins, and only traces of oil or wax. The greater part of the mineral matter also should have been removed. If proteins remain, they will combine with the chlorine of the bleaching liquors, giving rise to chloramines which will remain in the goods, and, gradually decomposing with the formation of hydrochloric acid, produce hydrocellulose and consequently tendering. They will, together with any unremoved pectins, also render the fabric less permeable than it should be to the bleaching liquors, both being precipitated on the goods as insoluble compounds by bleaching or acid liquors. Residual waxes, which are always coloured, will, after bleaching, work their way gradually to the surface, and cause loss of colour or discolorations. This is a very common cause of complaint.

The use of soft or softened water for the lye boil is absolutely essential. Hard water precipitates insoluble calcium soaps on the fibres. These render the fabric impermeable, and cause uneven dyeing. They also become yellow or brown when the fabric is stored, causing gradual loss of colour. The chemicals used must be of good quality. Impurities, such as sodium sulphate or chloride, retard both the saponification of fat and the hydrolysis of proteins. Table XLIV gives the approximate percentages of impurities found in cotton after boiling with caustic soda.

TABLE XLIV.—IMPURITIES IN COTTON AFTER CAUSTIC-SODA BOIL.

	No. 1.	No. 2.
Mineral matter . . .	0.26	0.42
Fat . . . . .	0.10	0.16
Fatty acids as soap . . .	0.16	0.26
Nitrogen . . . . .	0.05	0.07

In addition to the points already mentioned, there are certain others which must be attended to. Goods should not be allowed to come into contact with either iron or lead pipes in the keir. Both are liable to produce brownish stains. A dirty keir will act in the same way. In filling the keir the dilute lye should be made up outside the keir, and introduced at the bottom as described above. Under the name of *assistants*, such bodies as sodium silicate, sodium cresolate, Turkey-red oil, etc. are sometimes added to the lye, either to aid penetration or because they increase the detergent action of the soap formed by saponification of the oil. A mixture of sodium carbonate and hydroxide is also employed. Sodium carbonate dissolves proteins and pectins and assists in the emulsification of waxes and mineral oil, but it does not itself saponify fats, though it can form soaps with free fatty acids.

The lye which has been run off from the keir can be used again. If it is boiled with milk of lime, any sodium carbonate it contains is reconverted into sodium hydroxide, the soaps being also decomposed, giving insoluble calcium soaps and sodium hydroxide. Similarly, soluble sodium pectates give the insoluble calcium salts. If the precipitate is allowed to settle, the clear liquor can be drawn off, and used after the addition of sufficient caustic soda to bring it to the necessary concentration.

**The Lime Boil.**—This is a more complicated process than the caustic-soda boil. It is used generally in Lancashire, and particularly for the full white or *madder* bleach, the latter term being applied when the most thorough bottoming and avoidance of over-bleaching are demanded. The goods are first impregnated with milk of lime, then packed in the keir, and covered with more milk of lime. The boiling is conducted in the same way as with caustic soda. The effect of this is to dissolve the proteins, the saponifiable fats being converted into insoluble calcium soaps, and the pectoses and pectins into insoluble calcium pectates, both of which remain on the goods. Since no caustic soda is present, there is less danger of shrinkage and mercerization, or of the formation of oxycellulose.

After boiling, the goods are washed with water, and then treated with a dilute solution of sulphuric or hydrochloric acid ( $1^{\circ}$  to  $2^{\circ}$  Tw.). This decomposes the calcium pectates and soaps, forming the calcium salt of the acid used and free pectic and fatty acid. Naturally, hydrochloric is better than sulphuric acid on account of the greater solubility of its calcium salt, but sulphuric acid is much cheaper, and hence is generally used. After treating with acid (or *souring*), the goods are washed and returned to the keir, where they are boiled again with a solution of soda-ash (sodium carbonate) together with some rosin soap. This converts the free pectic and fatty acids into their soluble sodium salts, which can now be washed away with water, and this can be accomplished by boiling at ordinary atmospheric instead of high pressure.

The milk of lime used in the first operation is made by grinding up 56 lb. of quicklime with water, diluting the mixture to 100 gallons, and passing it through a sieve. The rosin soap is prepared by boiling 10 lb. of rosin with 30 to 35 lb. of sodium carbonate dissolved in water, and diluting the solution with about eight times its volume of water.

**Changes produced in Cotton by the Lye Boil.**—These are (i) loss of weight, (ii) loss of length, (iii) alteration of count, (iv) alteration of twist, and (v) increase in tensile strength. In well-boiled cotton the loss of weight amounts to from 5 to 7 per cent., and very little, if any, weight is lost afterwards. In order to estimate the true loss of weight, the percentage of water present in the goods, before and after boiling, must be known or determined by experi-

ment. The best way is to determine the condition weight of the goods before and after boiling. For example:—

A parcel of yarn weighed, when received, 105 lb. Determination of the percentage dry weight gave 89.50. Thus:

Percentage dry weight . . . . .	= 89.50
Regain $8\frac{1}{2}$ per cent. . . . .	= 7.61
Condition weight . . . . .	= 97.11

$$\therefore \text{Weight of yarn at correct condition} = \frac{105 \times 97.11}{100} = 101.96 \text{ lb.}$$

After boiling, the yarn weighed 95 lb., thus showing an apparent loss of 10 lb. The percentage dry weight was found to be 92.00. Thus:

Percentage dry weight . . . . .	= 92.00
Regain $8\frac{1}{2}$ per cent. . . . .	= 7.82
Condition weight . . . . .	= 99.82

Hence weight of boiled yarn at correct condition

$$= \frac{99.82 \times 95}{100} = 94.83 \text{ lb.};$$

$$\therefore \text{True loss} = 101.96 - 94.83 = 7.13 \text{ lb.}$$

The loss of length varies considerably with the conditions of boiling, but it need not be more than 2.5 per cent. The alteration in count depends upon the loss of weight and length. Anything which decreases the weight of a given length naturally increases the count. But true, not apparent, counts must be taken as the basis of comparison. Table XLV illustrates the effect of lye boiling on the count of cotton yarns:

TABLE XLV.—EFFECT OF LYE BOILING ON COUNT OF COTTON YARNS.

True Count before Boiling.	True Count after Boiling.
32	33.72
40	42.00
80	83.00
100	104.60
120	125.60

The alterations of twist are of two kinds. If the fibres have been subjected to any mercerizing action, the natural twist of the fibre will tend to be lost. But there is also an increase in the number of turns per inch, *i.e.* in the twist imparted during spinning. This is due to the shrinking and tightening of the yarn. An increase in tensile strength is always observed in boiled goods. If they are not stronger than before, there is some fault in the process.

**The Use of Organic Solvents.**—The weak spot in the lye-boiling process is its inability to remove completely the cotton waxes, and it has been noted already that if these are left in the goods they commonly cause discolorations. The cotton waxes have been referred to on p. 99. When one remembers that the natural fatty constituents of cotton include unsaponifiable hydrocarbon oils, and waxes only saponifiable by boiling glycerin and potassium hydroxide, it is not surprising that the lye boil is unable to remove them completely, even



though it has been brought to a high pitch of mechanical perfection. It is from a chemical point of view that it fails. Hence modern research has been directed towards the finding of a better process. Of the alternative methods available, the use of an organic solvent offers most advantages, and it seems likely that this method of removing the waxes will gradually become common. It was found, also, by Lumaden, Mackenzie and Fort, that extremely small amounts of oil or wax, such as are found in cotton boiled in the ordinary way, may inhibit *beetling* (a process in cotton-finishing) and render it almost futile. As a result of these experiments they patented a method for removing these oils and waxes by solvent extraction, as an alternative to lye boiling. Any of the types of apparatus described for wool are suitable for cotton. After degreasing, the proteins, pectins, and other soluble constituents still remain in the cotton. These are now, however, quite readily dissolved by boiling with a solution of sodium carbonate at ordinary pressure, and washing with water. It has been suggested also that they could be removed by treating the degreased goods with pancreatin, which, it is claimed, not only converts proteins into soluble peptones, but dissolves pectoses and pectins as well.

**Bleaching or Chemicking.**—Cotton loses a great deal of its colour during the lye boil, and for some purposes does not require further treatment. As a general rule, it passes from the washing machine, after the lye boil, to the bleaching or *chemicking* process. Bleaching powder and, to a limited extent, sodium hypochlorite are the only bleaching agents used for cotton. The chemistry of these has been described already.

**Preparation of the Bleaching Solution.**—The bleaching powder is ground in a mill, or rubbed through a sieve, into a stone or concrete extracting tank containing water at a temperature of from 75° to 80° F. (23.9°–26.7° C.). The mixture is then agitated thoroughly for about twenty minutes by means of a mechanical mixer, and allowed to settle. The sludge consists chiefly of lime, but in order not to waste bleaching powder it is again extracted with water, after running off the clear liquor to the chemic store tank. In this way a stock solution of bleaching powder is obtained which may have a density of from 5° to 15° Tw. Approximately 5 parts of bleaching powder to 100 of water are required to produce a solution of 5° Tw. For a bleaching bath this stock solution is diluted with water till it has a density of about 2° Tw. Concentrations up to 5° Tw. are sometimes used, but in the case of goods which are difficult to bleach it is safer to treat them twice with a weak than once with a stronger solution, owing to the danger of producing oxycellulose.

The quantity of sludge produced is variable, depending upon the quality of the bleaching powder. It may rise to 25 per cent. of the whole, and is commonly 10 per cent. This waste can be saved by treating the solution with chlorine gas, which can be liberated from cylinders as required. Liquid chlorine is supplied in 70-lb. cast-iron cylinders by the Castner-Kellner Alkali Co., Ltd. The chlorination of bleach liquors has the following advantages: (i) the liquor is at least 35 per cent. stronger than when it is simply extracted with water; (ii) the loss through incomplete extraction of sludge is prevented; (iii) there is practically no sludge to dispose of or to extract; and (iv) the capacity of the plant is increased. The chlorine gas is led into the bottom of the chlorinating tank through lead pipes, and issues through a number of small orifices, the liquor being meanwhile agitated. If the tank is not too shallow no chlorine is lost, and only about fifteen or twenty minutes are required for complete chlorination. Fig. 146 illustrates an extraction tank connected to cylinders of chlorine in the manner suggested by the Castner-Kellner Co.

*Determination of the Strength of Bleaching Solutions.*—The strength of bleaching solutions may be expressed in terms of

- (1) The Twaddell hydrometer scale.
- (2) Grams of available chlorine per litre of liquor, or shortly *grams per litre*.
- (3) Litres of chlorine gas per litre of liquor, or *chlorometric degrees*.

The Twaddell hydrometer is generally used in estimating the strength of a bleaching liquor, though here inaccurate in its indications. The only accurate way to determine the strength of the solution is to titrate it with decinormal

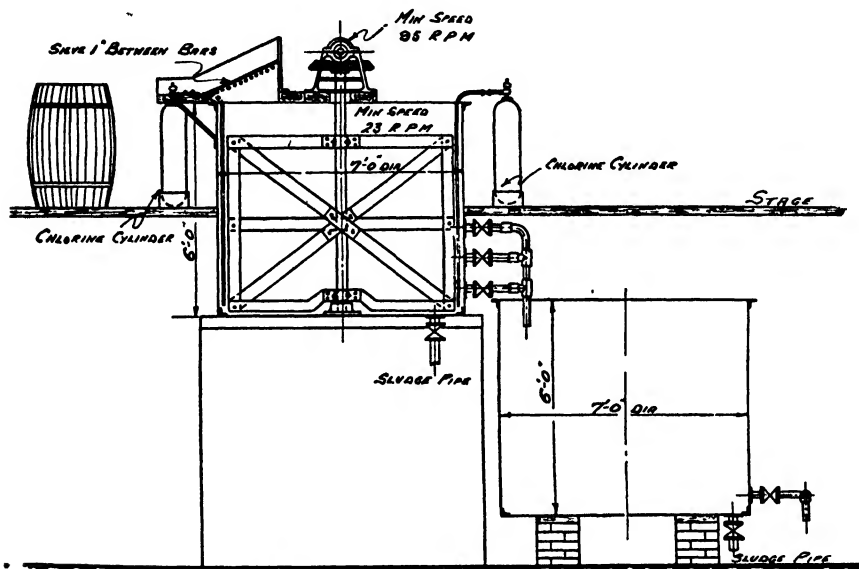
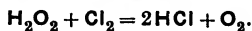


Fig. 146.—Castner-Kellner Chlorinating Tank.

sodium thiosulphate or arsenious acid. The method has been described on p. 230.

For the determination of chlorometric degrees, Böttler's method is suitable. It depends upon the fact that when a solution of chlorine or a hypochlorite is treated with hydrogen peroxide, oxygen is liberated:



The volume of the oxygen liberated is exactly the same as that of the available chlorine in the liquor. The test is carried out with the apparatus used for hydrogen peroxide (Fig. 113), the bleaching solution being placed in the tube. The rest of the details of the test are the same as for hydrogen peroxide.

Table XLVI (p. 298) shows the relation between the different methods of description.

**General Method of Bleaching.**—The bleaching powder solution is placed in a stone or cemented tank or well, beneath the bleaching tank (Fig. 147), which is made of stone or wood. The goods are passed from the washing machine into the bleaching tank by means of a wince. The chemic is then pumped from the lower to the upper tank, which it enters from perforated troughs resting on the top of the tank. This aerates the liquor as it falls on to the

TABLE XLVI.—CONVERSION TABLE FOR FRESH BLEACHING POWDER SOLUTIONS.

° Tw.	Specific Gravity.	Grams per Litre.	Chlorometric Degree.
0.5	1.0025	1.40	0.45
1.0	1.0050	2.71	0.86
2	1.0100	5.58	1.77
3	1.0150	8.41	2.67
4	1.0200	11.41	3.63
5	1.0250	14.47	4.61
6	1.0300	17.36	5.51
7	1.0350	20.44	6.5
8	1.0400	23.75	7.5
9	1.0450	26.62	8.3
10	1.0500	29.60	9.4
15	1.0750	45.70	14.5
20	1.1000	61.50	19.6
<hr/>			
0.3	1.0015	1	0.32
0.72	1.0036	2	0.64
1.1	1.0055	3	0.96
1.5	1.0075	4	1.27
1.8	1.0090	5	1.59
2.2	1.0110	6	1.91
2.5	1.0125	7	2.23
2.9	1.0145	8	2.55
3.1	1.0155	8.5	2.70

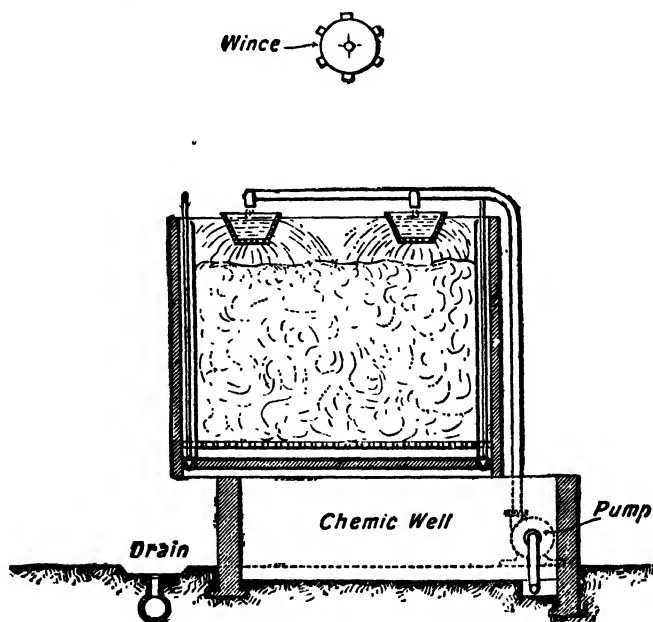


Fig. 147.—Bleaching Tank.

goods. When the goods are covered, the pump is stopped, and the liquor is allowed to drain back again into the well, air being drawn into the goods as the liquor leaves them. The process is repeated till the bleaching is complete. Other methods also are used. Instead of circulating the liquor, the goods may be kept in motion, being exposed alternately to the action of the bleaching liquor and to the air.

**General Conditions affecting Bleaching.**—The bleacher depends upon atmospheric carbon dioxide to develop the bleaching action of the chemic. This is why aeration is necessary. The action of carbon dioxide on bleaching powder solution has been described above. By aeration the bleaching action is developed very gradually, which is what the bleacher wants. Bleaching is accompanied by the disappearance of chlorine. The rate of absorption

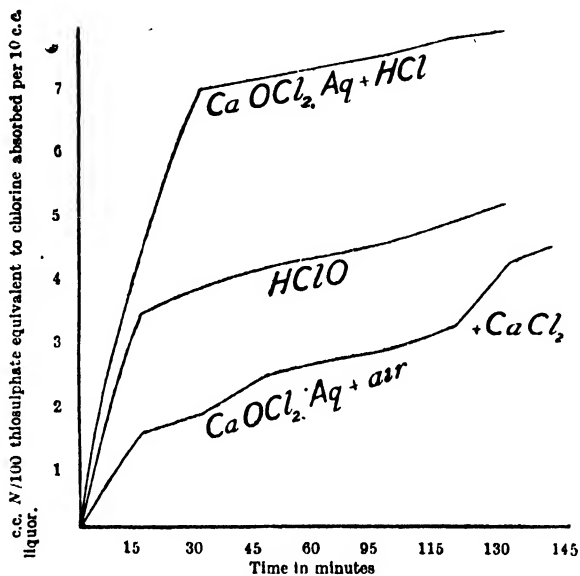


Fig. 148.—Absorption Curves.

can be determined by titrating portions of the liquor at intervals. If this is done, it will be found that the rate of absorption is at first rapid but soon becomes slower. This is seen in the curves shown in Fig. 148.

The bleaching action, under the influence of air, is accompanied by the deposition of calcium carbonate. If it is necessary to retard the rate of bleaching, an alkali, such as lime-water, may be added. On the other hand, a more rapid evolution of chlorine or hypochlorous acid can be brought about by the cautious addition of acids. A temporary stimulation of bleaching activity can be caused also by the addition of calcium chloride to the liquor.

Having regard to the retarding action of alkalis, it is important that the goods should be washed thoroughly out of the keir before passing them into the chemic.

The activity of a bleaching liquor is increased by allowing it to stand exposed to the air. This is owing to the absorption of carbon dioxide. Used liquors, if strengthened with more bleaching powder, are also more active than fresh liquors. This, according to Briggs (*J. Soc. Chem. Ind.*, 1916, 35, 78), is

due partly to the presence of calcium bicarbonate in solution, and of calcium carbonate in suspension. Such liquors are acid to phenolphthalein and alkaline to methyl orange. S. H. Higgins (*Bleaching*, Manchester, 1921, p. 78) found that old liquors give a precipitate with lime-water. Thus, when a fresh liquor is added, some of its dissolved lime is thrown down, and the alkalinity of the mixture is reduced. This disturbs the equilibrium of the system, and stimulates the production of chlorine or hypochlorous acid in the manner already described (Chapter XVII).

The temperature of bleaching is usually that of the atmosphere. Raising the temperature increases the rate, but with solutions containing more than 1 gram of chlorine per litre the action is too rapid, and over-bleaching (*i.e.* the production of oxycellulose) results. But Freiburger states that with concentrations not exceeding 1 gram per litre, the temperature may be raised to about 40° C. with safety. The advantages of this procedure are: (i) weaker solutions at higher temperatures bleach more quickly and efficiently than stronger solutions at lower temperatures; (ii) the time necessary for bleaching is correspondingly reduced; (iii) there is less danger of over-bleaching; (iv) a warm liquor penetrates the cotton more easily than a cold one, and reduces the danger of superficial bleaching; and (v) there is less likelihood of harshness in the finished goods, since the calcium carbonate produced is more granular than with cold liquors, and does not adhere so firmly to the goods.

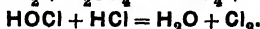
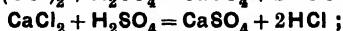
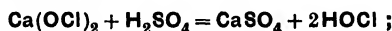
Freiburger's conclusions have been objected to on the ground that they were based apparently upon laboratory experiments only. But Trotman and Pentecost (*J. Soc. Chem. Ind.*, 1922, 41, 73T) confirmed the results by practical experience on a commercial scale.

The catalytic action of certain metals and their oxides on solutions of bleaching powder has been referred to. Particles of dirt and traces of iron or copper derived from machines are common causes of local over-bleaching, giving rise to tender patches. In this connection it should be remembered that lubricating oil and graphite derived from machines nearly always contain iron.

After bleaching, the goods should not be left lying exposed to the air, but should be washed immediately. Exposure to air will allow a dilute solution of bleaching powder to become sufficiently concentrated by evaporation to cause over-bleaching.

If the cotton has not been freed completely from proteins during the lye-boiling processes and subsequent washing, chloramines are produced by the bleaching liquor. Some of these, being insoluble, will remain on the goods, and cause subsequent tendering by the liberation of hydrochloric acid.

**Souring.**—After bleaching and washing, the goods are passed into a bath of dilute sulphuric or hydrochloric acid of about 1° Tw. strength. This is done simply to dissolve the calcium carbonate which has been precipitated on the fibres during bleaching. If this is not removed, it gives the cotton a harsh feel when dry. *The acid is not used to develop the bleaching action.* There should be practically no calcium hypochlorite left in the goods when they enter the acid bath (or "sour"). If there is, chlorine will be produced, and may result in over-bleaching:



The souring may be performed in the same apparatus as that used for bleaching, either the goods or the liquor being in motion. After souring, the

goods must be washed with water till every trace of acid is removed. If as little as 0.01 per cent. of acid is left, hydrocellulose, and consequently tenderness, are produced gradually when the dry goods are stored. Failure to remove the last traces of acid is a not uncommon cause of trouble.

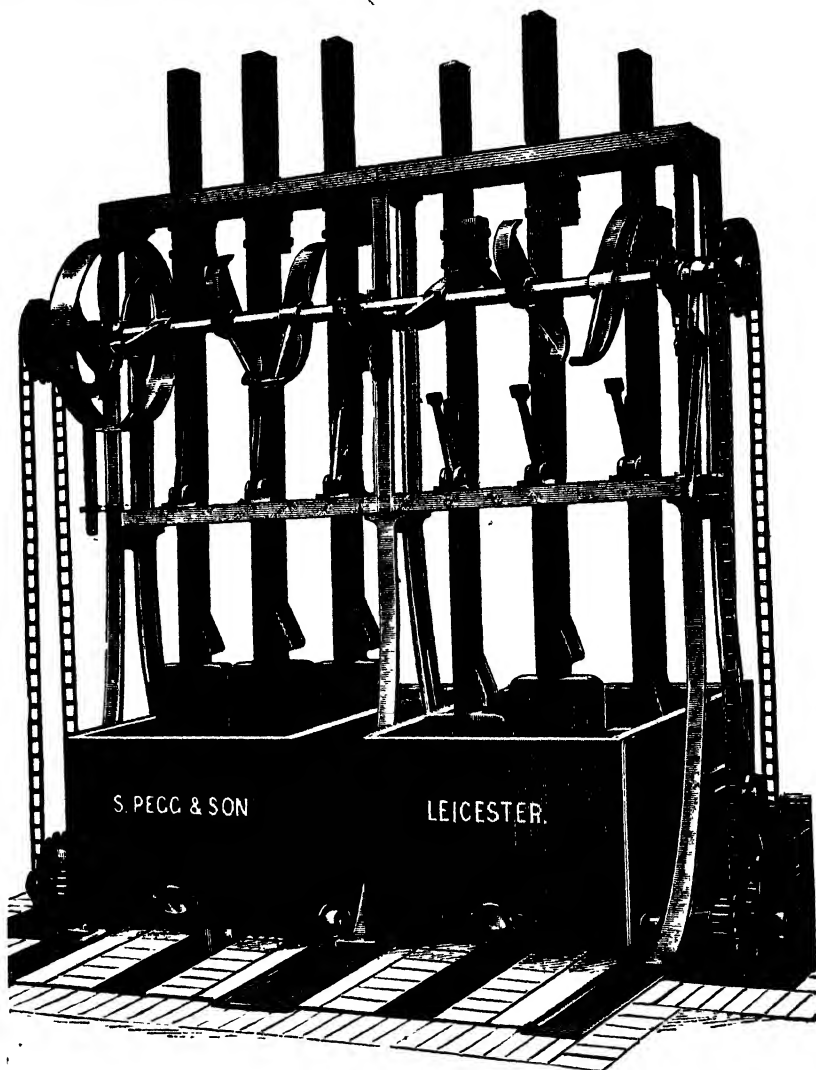


Fig. 149.—Improved Scouring or Washing Machine.

**Soaping.**—Finally, the goods may be soaped, and are sometimes treated with a dilute solution of an antichlor, such as sodium thiosulphate, to ensure complete freedom from chlorine. Soaping may be carried out in a washing machine or specially constructed dollying machine. A type of dolly is illustrated in Fig. 149. It consists of an oak tub or box, which is made to travel

backwards and forwards. The tub is provided with a perforated false bottom covering a shallow well with several outlets, which can be opened or closed while the tub is revolving. These lead into a circular trough, and thence to the drain or to a well for recovery of the dirty suds. The milling effect is produced by a row of beaters or fallers, analogous to those of a beetling machine, and capable of vertical movements, being lifted by the engagement of their tappets with cams mounted on a shaft at the back of the machine. The downward fall is produced by the weight of the beaters, but is prevented by a guide rail from quite reaching the bottom of the tub. The stroke can be further adjusted by altering the height at which the tappets are fixed. The cams are keyed to the shaft at different angles to distribute the load and impact on the fabric during its revolution; and the striking face of the beaters or fallers is splayed out and the edges are rounded so as to distribute the milling effect. The beaters may be put out of action by the hinged detents shown, or by inserting a peg through a hole in their shank when at the top of their stroke, the hole being bored at a point just above the lower guide rail, upon which the peg therefore rests and supports the beater. The degree of milling is regulated by the number of beaters in action, their weight, and the extent of their stroke.

The tub is surmounted by spray pipes for hot and cold water, and tanks containing fresh and recovered soap solutions. The bundles of lace, etc. are placed in the tub, which is then set revolving, and fed with water and soap. The beaters are then put into operation on one or both sides, and the degree of treatment is gauged by the number of *turns*, *i.e.* revolutions or traverse motions of the tub.

**Repetition of Processes.**—The chief difficulty in cotton-bleaching is to remove completely the impurities rendered soluble by one process before proceeding to the next, without damaging the goods. In the case of heavy materials, or those known to be difficult to bleach, a repetition of comparatively mild operations is found to give better results than a single treatment with a more drastic process, the impurities being removed in successive layers. Thus, while light goods, such as net, may be bleached completely by the methods described, in the case of heavy cloth, repetition of some or all of the processes is necessary to give what is called a *full* bleach. This will be understood better from a study of the following examples:—

—“*Madder*” Bleach for Heavy Cloth.—The succession of operations is

- (a) Singe, steep, and wash.
- (b) Impregnate with milk of lime and pass into the keir.
- (c) Boil for eight hours at 20 lb. pressure, and wash off in keir and through washing machine.
- (d) Soak in hydrochloric acid of 2° Tw. strength, and wash through machine into keir.
- (e) Boil under pressure (10 to 15 lb.) with sodium carbonate and rosin for eight hours. Wash off in keir, and then through washing machine into the chemic tank.
- (f) Circulate the chemic (about 1 gram per litre of chlorine) for two to three hours. Drain off chemic, and pass through washing machine into the sour.
- (g) Circulate the sour (1° Tw.) for about two hours. Then wash through washing machine into keir.
- (h) Boil under pressure with sodium carbonate and wash into chemic tank.
- (i) Circulate chemic (about 2 grams per litre of chlorine) for two hours and wash.

(j) Sour as before and wash again.

*Caustic-soda Method for Heavy Goods.*—(a) Singe, steep, and wash.

(b) Boil under pressure of 30 to 40 lb. with caustic soda, using about 3 per cent.  $\text{Na}_2\text{O}$  on the weight of the goods, and wash back into keir.

(c) Repeat the lye boil and wash into chemic tank.

(d) Circulate chemic (2 grams per litre) for two hours and wash into sour.

(e) Circulate sour (1° Tw.) for two hours and wash into keir.

(f) Boil at ordinary pressure with 1 to 2 per cent. of sodium carbonate for four hours and wash into chemic tank.

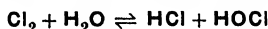
(g) Circulate chemic (2 grams per litre) for two hours and wash into sour.

(h) Circulate sour for two hours and wash.

**Sodium hypochlorite** is used in exactly the same way as bleaching-powder solution. Owing to the fact that soluble sodium carbonate is produced by the action of carbon dioxide on either sodium hypochlorite or hydroxide, the bleaching action of sodium hypochlorite is developed rather more slowly than that of bleaching powder. Since no insoluble decomposition products are produced, it is useful for goods where any trace of harshness must be avoided. A sour is not essential, though commonly used. Sodium-hypochlorite liquors are specially suitable for using warm, for goods that, in the ordinary way, are difficult to penetrate. A little Turkey-red oil is a useful addition in such cases. The analysis of sodium-hypochlorite liquors is carried out in the way described for bleaching-powder solutions.

The preparation of sodium hypochlorite has been described on p. 224. Bleaching solutions of any desired strength can be made very easily by passing chlorine gas into a cold dilute solution of sodium hydroxide. The alkaline solution is placed in a tank provided with a stirrer, and the chlorine is led in from the cylinder by a delivery pipe reaching to the bottom, and delivering the gas through a number of small orifices in the horizontal or spiral end of the pipe. The hydroxide must not be entirely decomposed, or the liquor will be too unstable. It is best to leave a residual alkalinity of about 0.2 per cent.

**Bleaching with Hypochlorous Acid or Chlorine-water.**—Ornstein (Brit. Pat. 147,069—1920) claims that when chlorine gas is led into water, if not more than from 0.1 to 0.2 gram of chlorine per litre is used, hypochlorous acid is produced but no free chlorine. That is, the equation:



proceeds only from left to right at ordinary temperatures. When the concentration exceeds 0.3 per cent., the amount of hydrochloric acid present is sufficient to alter the equilibrium of the system, and the action then proceeds also from right to left, *i.e.* as much hypochlorous acid reverts to chlorine as is produced over and above the maximum concentration for equilibrium. But Ornstein claims that dilute solutions of hypochlorous acid prepared in this way are suitable for bleaching cotton. If the hydrochloric acid is removed as it is produced by means of a base, such as calcium carbonate, which is not decomposed by hypochlorous acid, more concentrated solutions of the latter acid can be obtained. Solutions of hypochlorous acid obtained in this manner, adjusted to a strength of 1 gram of available chlorine per litre, were found by the authors (*J. Soc. Chem. Ind.*, 1923, 42, 2r) to give excellent whites on cotton and also to bleach more quickly. The rate of the bleaching action compared with that of ordinary bleaching powder solution is seen in Fig. 148. When hypochlorous acid is used, an acid bath may be dispensed with, since no calcium carbonate is formed.



**Hydrogen peroxide and sodium peroxide** are very rarely used for bleaching cotton, but they can be employed in the same way as for wool.

**Potassium permanganate** gives excellent whites with cotton. From 0.2 to 0.5 per cent. is required, depending upon the nature of the cotton and the thoroughness of the boiling process. The following method gives good results: The boiled cotton is wetted down in sulphuric acid of about 5° Tw. strength, and then completely covered with the same acid. From 0.2 to 0.5 per cent. of potassium permanganate (on the weight of cotton) is dissolved in water, and added to the bath in portions. The goods are worked occasionally to ensure circulation of the liquor. The bleaching action is generally complete in about two hours. At the end of this time the goods are removed, and washed thoroughly. Any of the other processes already described may also be used. The combination of a permanganate with a peroxide bleach is very efficient. In this case, the cotton is soaked in a cold solution of permanganate for some hours. It is then rinsed with cold water, and placed in a weak bath of hydrogen peroxide containing a little sulphuric acid. This reduces and dissolves the deposited oxides of manganese, liberating oxygen, which further bleaches the cotton.

**Bleaching Coloured Goods.**—White goods with coloured patterns or borders often have to be bleached, leaving the colours unattacked. In these cases special precautions are necessary. The exact method adopted must depend upon the degree of fastness of the dyes used. As a rule, therefore, the first thing to be done is to test the fastness of the coloured portions to the various processes, and modify the latter when it is necessary. The lye boil may have to be carried out with sodium carbonate instead of caustic alkali and at atmospheric pressure. Or, sometimes, a scour with warm soap and water is all that the colouring-matter will stand. Weak solutions of bleaching powder of 1° Tw. or less may be employed, and their activity limited by the addition of small quantities of lime-water. No general methods can be given, but examples will be found in Chapter XXIII of Trotman and Thorp's *Principles of Cotton Bleaching*.

**Testing Bleached Cotton.**—Well-bleached cotton should consist of practically pure cellulose. Its tensile strength should be at least as great as that of the original cotton; the white should be pure and durable; the feel should not be harsh; and no acid, residual chlorine, or unremoved non-cellulose impurities should be present. Faults, in any of the processes, sometimes cause immediate damage, but in other cases the damage develops only when the goods are stored.

The general analysis of bleached cotton includes the following determinations:—

(1) *The tensile strength* is tested by one of the machines described in Chapter VIII. It has been stated that the lye boil increases the tensile strength. The bleaching process, if conducted carefully, should never reduce it again below that of the original cotton.

(2) *Ash.*—This is determined in the usual way, by incinerating about 5 g. in a platinum or silica dish. The ash of a well-bleached cotton should be white or grey in colour and not above 0.1 per cent. Excessive ash generally means incomplete removal of the calcium carbonate produced during the bleaching process.

(3) *Oil.*—A weighed quantity (about 5 g.) of the cotton is dried, and extracted with petroleum ether in a Soxhlet extractor for about four hours. The solvent is then evaporated off, and the residual oil dried and weighed. It should not exceed 0.01 per cent.

(4) *Soaps*.—The extracted cotton is soaked in cold dilute hydrochloric acid for about three hours, and then washed with cold distilled water and dried. When dry it is again extracted in the Soxhlet extractor to remove the liberated fatty acids.

(5) *Loss on Boiling with Alkali*.—Cotton which has been properly lye-boiled contains but little matter soluble in alkali, unless it has been over-bleached. This test is carried out by drying 5 g. of the sample, and weighing it in a stoppered weighing-bottle. The weighed cotton is then boiled gently for about two hours in a 2 per cent. solution of sodium hydroxide, and washed with hot water till nearly free from alkali. Next, it is treated with dilute acetic acid, again washed and dried, and reweighed in the weighing-bottle. The loss of weight is determined by difference. It should not exceed 1 per cent.

(6) *Qualitative tests* for hydrocellulose and oxycellulose, and for the detection of free acid, are carried out as described in Chapter IX.

(7) *Copper Value and Methylene-blue Number*.—See Chapter IX.

(8) *Freedom from chlorine* is ascertained by soaking the sample in a dilute, slightly acid solution of potassium iodide and starch.

**Damage and Defects due to Bleaching.**—Bleached cotton goods not infrequently show defects, either immediately or after storing. These cause considerable trouble, and it is often very difficult to trace them to their source. Among the most important defects met with are—

(1) Mechanical damage caused by machines which require overhauling. Uneven bowls of a mangle or washing machine may be cited as an illustration.

(2) Small holes caused by live steam in the keir.

(3) Metallic stains which may be caused by contact with iron or lead pipes.

(4) Tenderness or breaking down of the material in the lye boil. This may be due to the production of oxycellulose by the presence of air, or by exposure of the goods to air before washing out the lye. It may be caused also by local shrinkage, which may produce distortion of pattern effects or rupture of the weaker threads. The authors have, in some cases, traced these defects to the following cause: In filling up a keir it is a common, but faulty, custom to put a few bucketfuls of concentrated caustic soda into the well and then, after packing, fill up the keir with water. This water simply lies on the surface of the strong lye. When circulation is started, the concentrated lye is brought into contact with the goods, and causes shrinkage before it has time to become diluted with the water in the keir. If the goods are not well packed, and lines of least resistance are present, through which the concentrated liquor can flow, this effect is still more likely to be produced. In such cases the shrunk portions will often give a positive reaction for mercerized cotton.

(5) Tenderness due to over-bleaching. This is generally caused by oxycellulose. Its production may be traced to the use of too strong or too active a liquor, or to the presence of catalysts such as iron or copper, in the goods. A less frequent cause is the production of chloramines owing to proteins not having been removed completely by the lye boil.

(6) Tenderness due to acids. This is the chief cause of trouble. It comes from incomplete washing of the goods after souring. In dressed goods it may be caused also by the use of salts, such as calcium or magnesium chloride, which dissociate with the liberation of hydrochloric acid. In these cases the tenderness is developed or increased by ironing.

(7) Discolorations or stains due to the presence of calcium or magnesium soaps, which become yellow or brown upon drying and exposing to the action of air.



Fig. 150.



Fig. 151.



Fig. 152.



Fig. 153.



Fig. 154.



Fig. 155.

Figs. 150 to 155.—The Congo-red Test. (After T. B. Bright.)

Fig. 150.—Normal hairs, undamaged.

Fig. 152.—Slight mechanical damage.

Fig. 154.—Severe mechanical damage.

Fig. 151.—Thick-walled hair, undamaged.

Fig. 153.—Damaged during teasing out.

Fig. 155.—Damaged by heat.

(8) Discolorations due to unremoved oil and wax. This is one of the common causes of trouble. It is due, as indicated before, to incomplete lye boiling or to the presence in the goods of mineral oil, which the lye boil is incapable of removing. Unremoved oil or wax may not be apparent directly after bleaching, but when the goods are stored it works its way to the surface gradually, giving the goods a yellowish tint. Liability to yellow on storing may be detected by steaming a piece of the fabric for some time at ordinary pressure, or for a short time in a small autoclave.

(9) Discolorations, and even tenderness, may be caused by the growth of bacteria or moulds.

Mechanical damage may be identified by Bright's Congo-red test. The hairs are teased out, swollen in 11 per cent. sodium hydroxide solution, and stained with Congo Red. The appearance of damaged hairs is seen in Figs. 152 to 155.

*The Lewis test* for chemical damage is useful: The hairs are treated on a microscope slide with a solution of sodium zincate,  $\text{Na}_2\text{ZnO}_2$ . After a few minutes the excess is removed with filter-paper, and water is drawn through. Undamaged or mechanically damaged hairs have a definite outline, the ends being swollen to a dumb-bell shape. Slightly damaged hairs are mostly the same, but a few are more swollen and less definite in outline. Hairs damaged sufficiently to cause weakness or holes have blurred edges and ends, and may be partly dissolved. In cases of bad damage, a shapeless mass is produced. The reagent is made by precipitating zinc hydroxide with ammonia from a boiling solution of zinc sulphate, washing until free from sulphate, and dissolving in hot 60° Tw. sodium hydroxide solution until it is saturated. After cooling, the solution is filtered through glass-wool.

## CHAPTER XXIII.

### COTTON-FINISHING.

AFTER the goods have been bleached and washed, they are transformed from the rope form to the open width, and at the same time they are straightened out, mechanical strains or distortions are corrected, and the original width is recovered. This is effected by means of an apparatus known as a *scutcher* (Fig. 156), though other methods, such as the use of scrimp rails and stenters and rotary expanders, are employed.

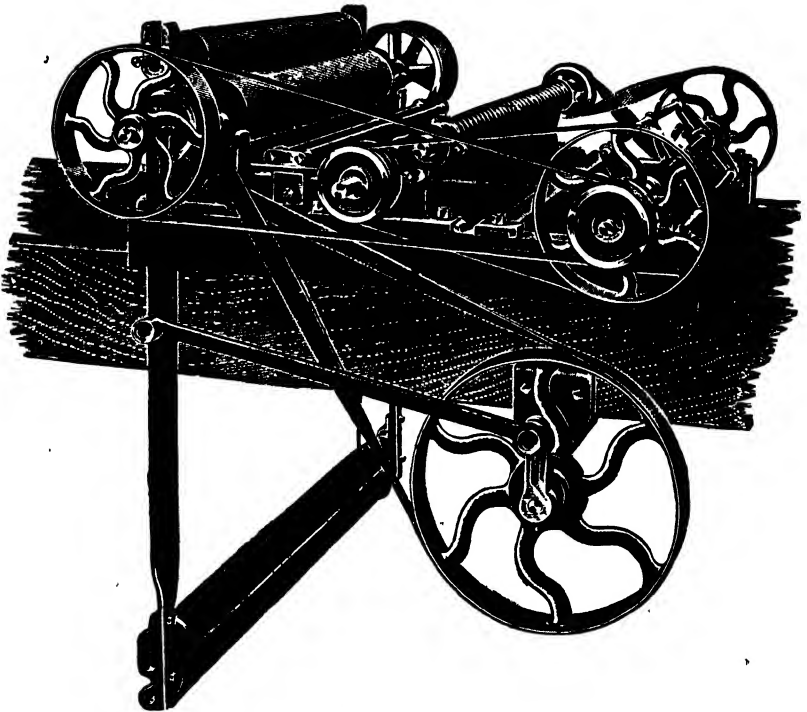


Fig. 156.—Scutcher.

After leaving the scutcher, the cloth is usually treated in the open form with a hot wash in a water mangle to remove the last traces of dirt, the pressure applied imparting, at the same time, some degree of permanence to the recovered width. The treatment in the water mangle may be adjusted to close up the threads and smooth out the surface of the cloth, thus assisting

in the production of the final finish. A *thready* appearance may also be produced during the mangling process by means of *chasing*. This implies the re-entry of the cloth through one or more of the nips through which it has already passed, so that there are two layers of cloth, one of which is passing through for the first time, and the other for the second. The process may be

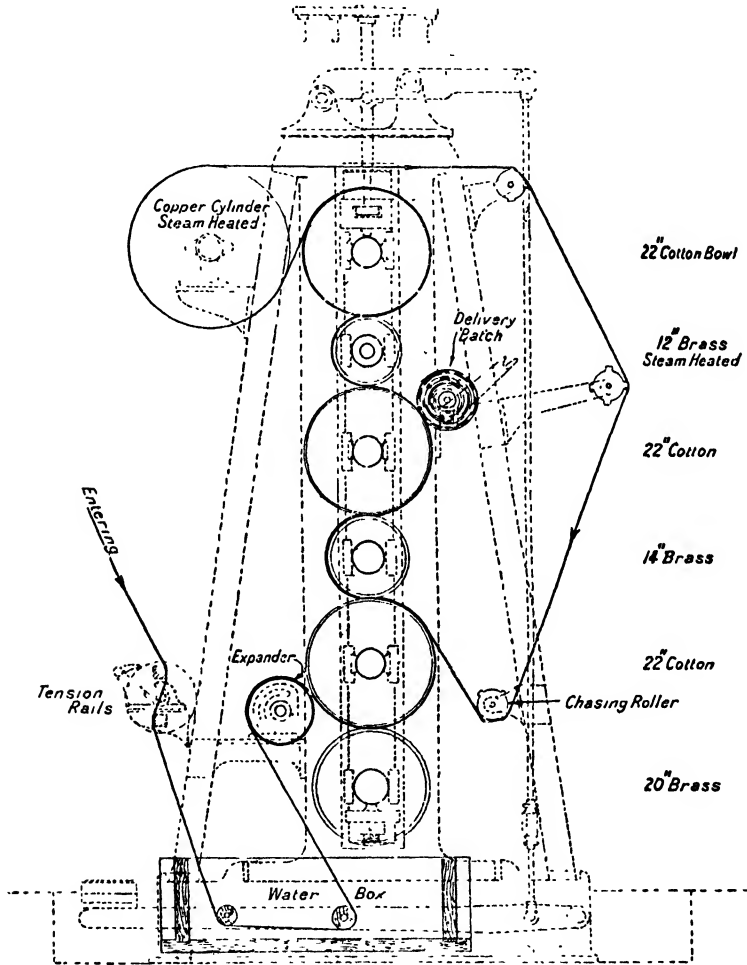


Fig. 157.—Six-bowl Water Mangle.

extended to three or four layers. The threads on the opposing surfaces are pressed against each other, and acquire a rounded form and appear to be embossed on the fabric. The magnitude of the pressure, the composition and arrangement of the bowls, and the method of threading up the cloth are the chief factors which determine the mechanical effect produced. In the six-bowl mangle illustrated in Fig. 157 the application of heat to the upper brass bowl and the copper cylinder swells the thread while still damp, and enhances the subsequent closing-up effect.

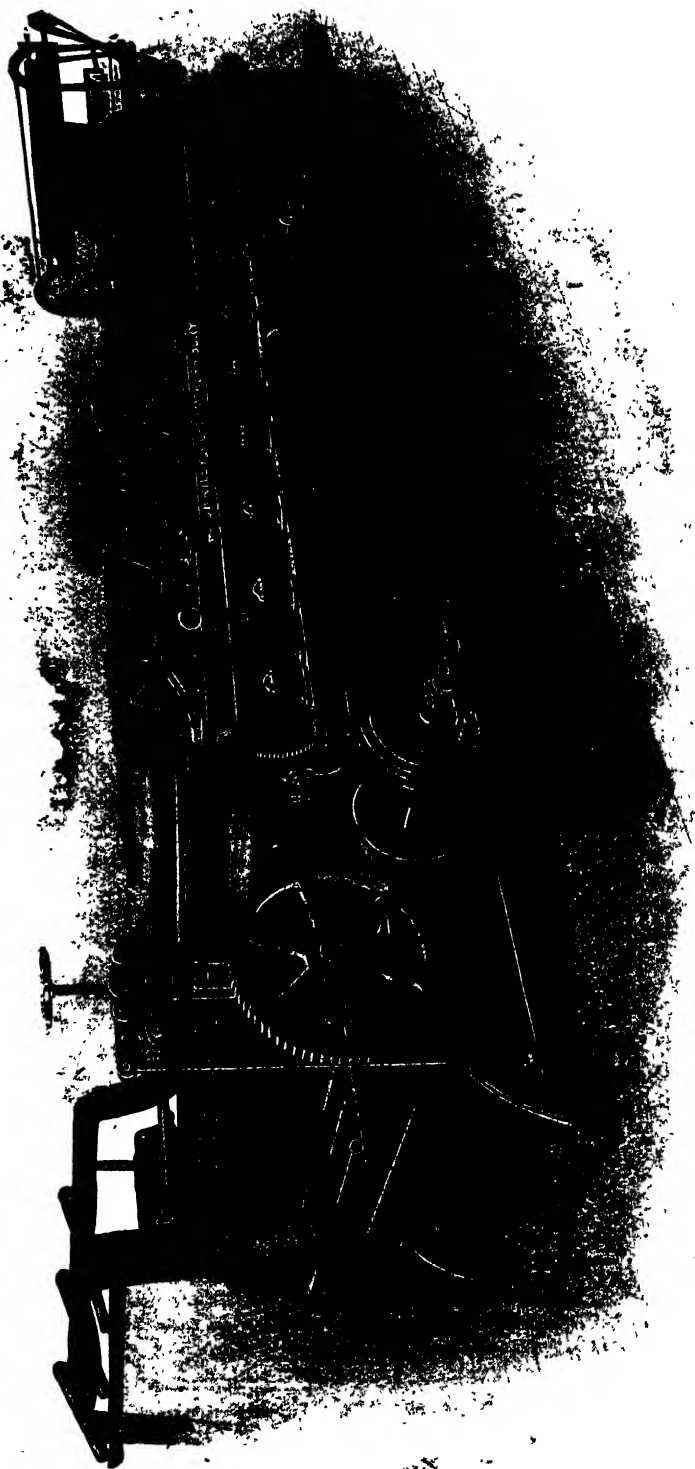


Fig. 158.—Finishing Range.

The treatment of the goods after the opening-out process depends upon the type of finish required. Finishes may be classified as—

(1) *Pure finishes*, where no chemical assistants are used but only mechanical effects. Goods for printing or dyeing may be simply dried after opening out. Others, such as calico, may require a particular surface effect, but both would be pure or *unassisted* finishes.

(2) *Assisted Finishes*.—In these cases some binding or stiffening material is added to the cloth to give additional effect to the subsequent mechanical processes employed, or to affect the feel of the finished cloth.

(3) *Stiffened Finishes*.—In these finishes the goods are heavily treated with stiffening, binding, or weighting materials, the cloth being sometimes almost disguised.

**Drying previous to Finishing.**—After the mangling process, the goods are generally completely or partly dried before applying the finish. A drying machine made by J. H. Riley & Co., Ltd., of Bury, is shown in Fig. 158. It consists of a series of steam-heated rollers of tinned iron or sheet copper. The cloth is fed on to the machine through tension and scrimp rails, or to an expander, to keep it straight. It then passes consecutively over and under the heated cylinders, and is finally rolled on to a drum.

The condition, or degree of moisture left in the cloth, has an important effect on the subsequent processes. The effect of complete drying is to harden the fibre. A moderate amount of moisture swells and softens the threads and increases their tensile strength and elasticity. The goods are either dried up to the required condition in the drying machine, or completely dried and then conditioned, or damped, by means of a *damping* or *dewing* machine. In Downham's machine a mist or spray is produced by the rapid rotation of a fine bustle roller, which dips into water and throws it off tangentially.

## PURE OR UNASSISTED FINISHES.

The above processes of opening out, washing in the mangle, recovering width, and straightening out, followed by drying up, may complete the finishing operations. But, apart from dyeing or printing, certain surface effects are generally required. The chief processes employed for this purpose are beetling, calendering, and schreinerizing, which will be described briefly.

**Beetling.**—The chief effects of this process are

- (1) Closing up, and thus eliminating the spaces between adjacent threads.
- (2) Producing a bright hard finish, or one that is relatively dull, clothly, and thick.
- (3) Increasing the width of the cloth.
- (4) Leaving a surface effect known as a *water-mark*.

These effects are not produced simultaneously. The beetling process consists in subjecting the cloth to a rapid succession of blows applied independently and consecutively across its surface by a series of hammers or fallers. Each faller delivers about seventy-two blows per minute, but each successive blow strikes the surface at a different point owing to the progressive and lateral movement of the cloth. The faller, which is made of wood, has a smooth, rounded end. This limits the contact with the cloth to a small area, within which the more centrally disposed threads sustain a vertical pressure and the outer ones a more oblique one, tending to cause their lateral deflection. The combined effect of these lateral impressions is to produce a rolling kind of motion, which tends to round the threads. The vertical blows, on the other



hand, cause flattening and extension. Thus the final result is a combination of the two effects.

There are various forms of beetling machines. That made by Messrs. A. Edmeston & Sons, Ltd., is shown in Fig. 159. It consists of a row of beechwood fallers resting between two pairs of rolled-steel guide-rails, ground and glazed on their working surfaces. Lateral play between the fallers is reduced to a minimum by planed distance-pieces. The *wiper*, or compound helical cam, which raises the fallers by engagement with their projecting tappets, consists of a series of three-armed cams mounted on a common shaft. The shape of the cam is designed in such a way that, at the beginning of the lift, the point of contact between it and the tappet of the faller is at that part of the working surface of the wiper which has the least velocity. This reduces the shock which inevitably occurs in overcoming the inertia of the faller. At the top of its rise, the engagement between the tappet and wiper arm ceases, and the faller drops by its own weight and delivers a blow to the cloth beneath. The helical method of assembling the unit cams causes the fallers to drop consecutively and not together. The blow is almost instantaneous, as the faller rebounds immediately from the cloth. The cloth during treatment is wound and rewound on the rollers shown in the illustration.

The results produced by beetling are affected by many conditions, among which are the amount of moisture the cloth contains, its temperature, the duration of the treatment, and the purity of the cloth. Fort (*J. Soc. Dyers Col.*, 1921, **37**, 162) found that the result was affected greatly by the presence of residual cotton waxes. The occurrence of as little as 0.1 per cent. of fatty matter, and sometimes even less, was found by him to be the cause of futile attempts to obtain a good beetle finish. But pieces which do not respond well to beetling can be treated quite satisfactorily if they are previously extracted with a volatile solvent.

The same author (*J. Soc. Chem. Ind.*, 1918, **37**, 121A) investigated also certain causes of mechanical disintegration of cotton fabrics which may be produced during beetling. Owing to the breaking of a traverse, the hammers fell continuously on the same sector of the cloth. Although the cloth had not been in any way damaged during bleaching, it broke down gradually, and in less than half an hour was ruined. The action was accompanied by loss of conditioning moisture and rise of temperature, and a large deposit resembling lumps of starch was obtained, which was crushed easily to a fine smooth powder, with a slight tendency to break into layers. The powder had the chemical properties of cellulose, and gave negative tests for hydrocellulose and oxycellulose, but the microscopic structure was quite different from that of merely shredded cotton.

Cross and Bevan, who examined the powder, found that it contained a large amount of an alkali-soluble modification of cellulose known as  $\beta$ -cellulose. The interesting point is that the change could have been produced only by mechanical or physical causes.

**Calendering.**—In this process the prepared and dried cloth is subjected to pressure between rollers or bowls of various kinds. The effects produced depend upon the nature and sequence of the nips, the temperature, and the nature and preparatory treatment of the cloth. These effects may consist in producing either a particular surface appearance or a particular feel. The former include such effects as glazing or brightening, closing up or producing a thready appearance, embossing or flattening. Among the latter are smoothness, hardness or softness, and a thready feel.

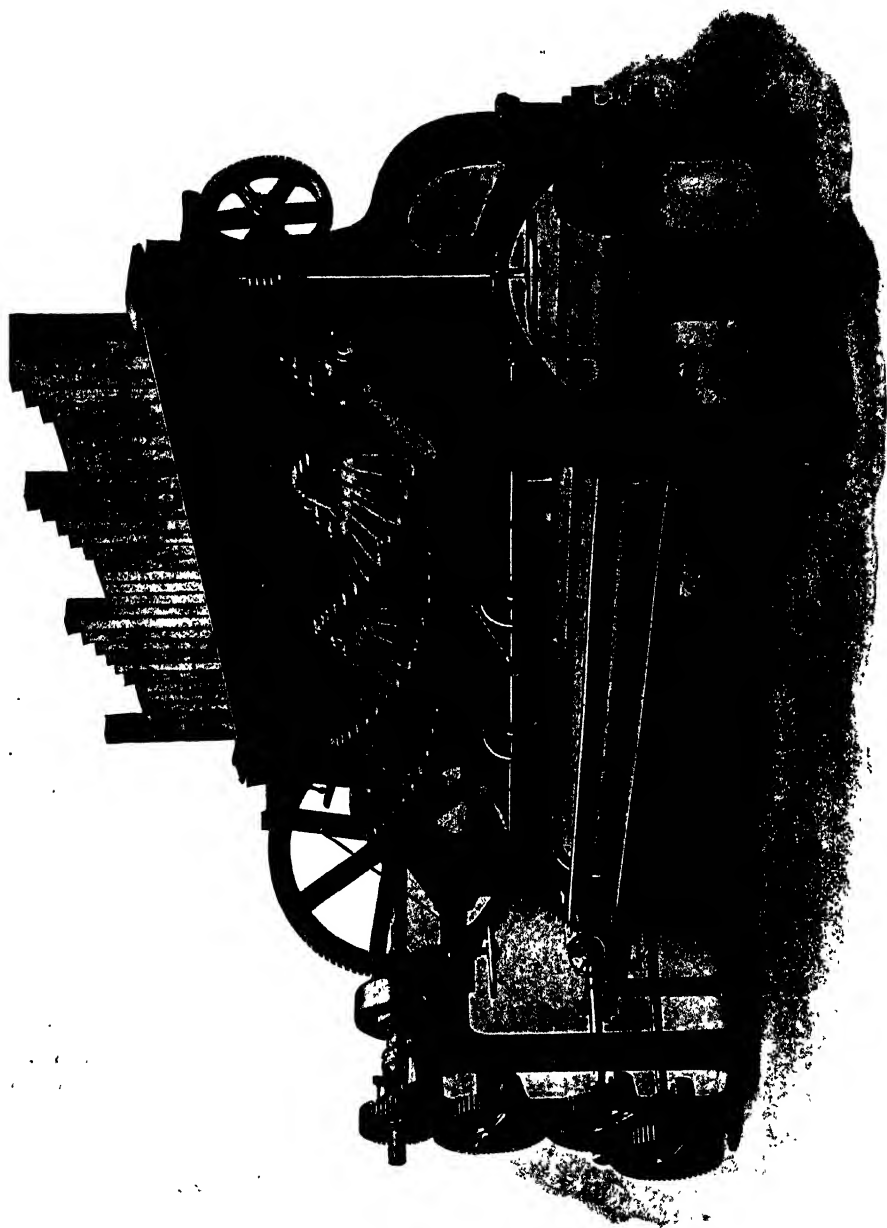


Fig. 159.—Beetling Machine.

Fig. 160 illustrates a type of calender made by Messrs. A. Edmeston & Sons, Ltd., which is suitable for the usual kinds of work known as *swissing* and *chasing*. Swissing consists in running the cloth straight through the nips

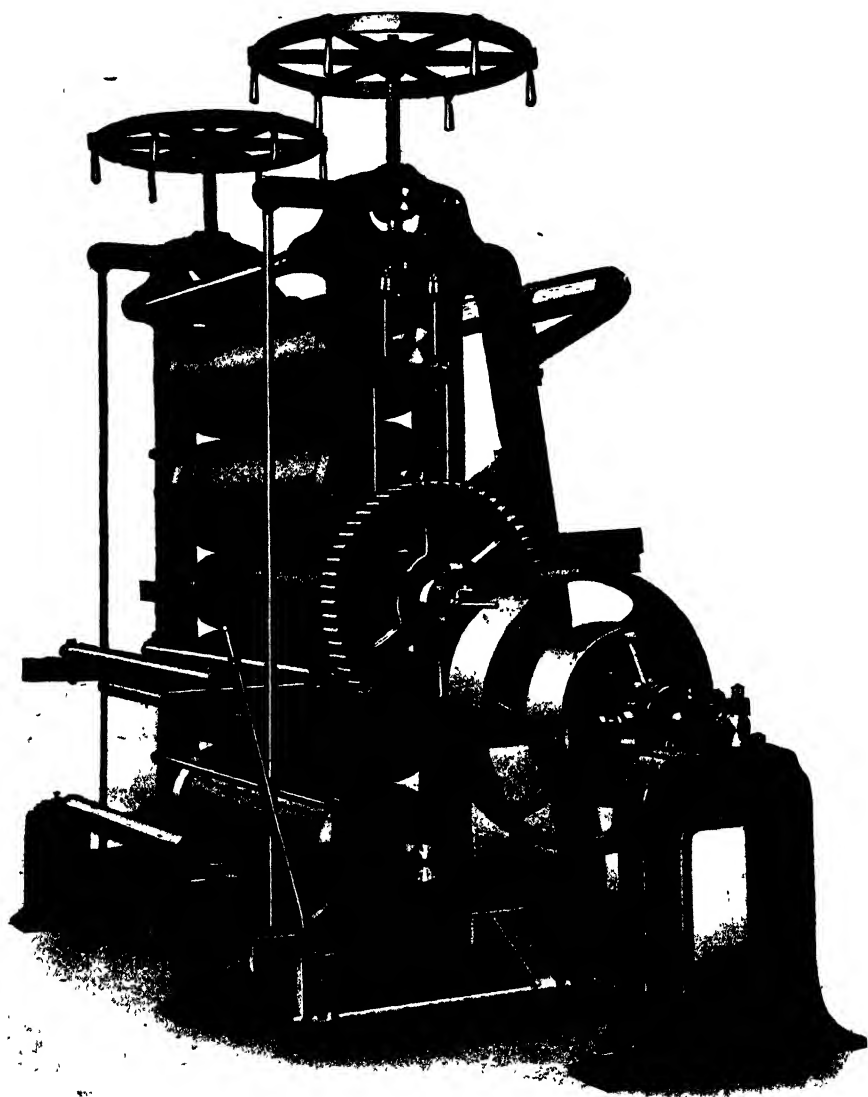


Fig. 160.—Five-bowl Chasing and Swissing Calender.

in series, and represents the normal method of calendering, designed to smooth and brighten the cloth, to close up the threads by flattening them, and produce either a hard or a mellow finish. Chasing has been explained already in

connection with mangles. It produces, as in mangling, a thready appearance, as well as closing up the threads, and gives firmness as distinct from hardness.

The number of bowls in a calender may vary from three to twelve, those containing three, five, and seven being more commonly used. The bowls may be either *metal* or *soft*. The latter are metal bowls covered with layers of cotton or paper. The sequence in which these are arranged varies according to the finish required. For example, to smooth slightly and brighten the

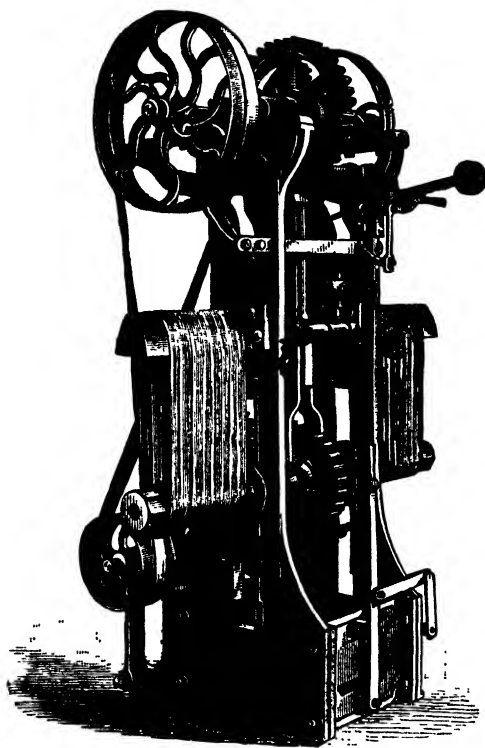


Fig. 161.—Improved Hank-stretching Machine.

surface of light goods, a small brass bowl between two cotton ones may be used, the cloth being run through dry. The bowls may revolve at different speeds to produce a polishing effect or friction. They may also be used either cold or hot. In the latter case they are generally heated by means of steam.

**Yarn-finishing.**—Bleached yarn is commonly conditioned by exposure to the air or by spraying. It is then straightened out by hand, and pressed into bundles. But it may also be stretched or straightened by means of a machine, and calendered or polished. A yarn-stretching machine is shown in Fig. 161, while Fig. 162 illustrates a suitable form of calender. In the latter, which consists of two cotton and one cast-iron (top) bowls, the hank is introduced by removing the middle bowl and threading one end round it. The threads are spread out evenly over the surface, and the same applies to the

other end, which is, however, threaded over a free guide roller. The hank thus rotates round the two as an endless band, and sustains one nip between the two cotton bowls and a second between the middle cotton and upper metal bowls

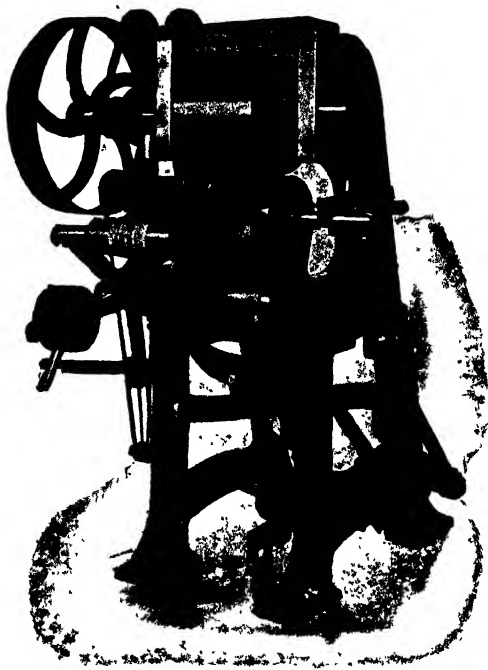


Fig. 162.—Improved Yarn-preparing Machine.

The polishing of sized yarn is effected by causing it to rotate round wince wheels, against which a series of stiff brushes, mounted on a drum, revolve in the opposite direction.

#### ASSISTED AND STIFFENED FINISHES.

The goods, after being bleached and washed, are opened out, twists or strains are corrected as in the case of pure finishes, and the goods are dried or partly dried. They are then treated with the finishing mixture, and are finally subjected to such mechanical processes, including those described already, as are necessary to produce the desired surface or feel. The exact composition of the finishing mixture used is determined by a combination of experience, knowledge of the chemical and physical properties of the bodies used, and experiment. The various substances used may be classified as follows:—

- (1) *Stiffening and binding materials*: the starches, dextrin, glue and gelatin, casein, gums, algin, Iceland and Irish moss, carnaïba wax.
- (2) *Filling materials*: gypsum, calcium carbonate, magnesium sulphate, barium sulphate, china clay or kaolin, talc, and other silicates.
- (3) *Softening agents*: soaps, oils, and waxes.
- (4) *Deliquescents*: magnesium and zinc chlorides, glycerin.

(5) *Antiseptics*: boric acid, borax, phenol, formaldehyde, zinc chloride, salts of copper.

(6) *Blueing materials*: smalt, ultramarine, coal-tar dyes.

(7) *Fireproofing agents*: metallic oxides, phosphates, tungstates, borates, silicates.

(8) *Waterproofing agents*: insoluble soaps, oxidized or oxidizable oils, gelatin tannate or formaldehyde-gelatin, paraffin or other wax, rubber, cellulose acetate.

This classification is general, referring only to the chief characteristics of the bodies named. Some of the agents perform additional functions, or may be included in more than one class; thus filling agents have their individual effects on the appearance of the cloth and its feel. Deliquescent and deliquescent antiseptics are simultaneously softening and sometimes weighting agents.

### Stiffening and Binding Agents.

**Starch** is by far the most important of these. The starches used in finishing are chiefly wheat, maize, potato, rice, and cassava. Tapioca and sago are also employed for certain purposes

Starch is very widely distributed in the vegetable kingdom, occurring chiefly in various grains, seeds, roots, and tubers. It belongs to the carbohydrate group of chemical compounds, and has the formula  $(C_6H_{10}O_5)_n$ . It always occurs in the form of granules, which for different starches have different characteristic shapes and structures. As a rule, starch granules have a stratified appearance, with a small point or *hilum* around which the strata are laid down. The different layers contain different amounts of water. The hilum is always rich in water, and each layer alternately contains more or less water, the outer being the poorest in water and the richest in substance. As a consequence of the increasing proportion of water from the outside to the hilum, fissures radiating from the hilum to the periphery are often formed. If starch granules are soaked in alcohol, which abstracts the water, the stratification disappears. The granules consist of two substances, *granulose* and *starch cellulose*, together with minute quantities of nitrogenous constituents and oil. The starch cellulose occurs chiefly in the outer layers. It is much more resistant than granulose, and thus forms a protecting coat for the granules. This may be ruptured by boiling water, or by mechanical grinding, and the granulose liberated. Starch cellulose is less soluble than granulose. Thus, when starch is treated with dilute acids or alkalis, the granulose is first attacked, and, with care, it is possible to leave the cellulose behind. But it must be stated that work by Harrison (*J. Soc. Dyers Col.*, 1916, **32**, 40) tends to prove that there is really no difference in composition between the outer and inner layers of the granule, except that the former is more resistant to hydrolysing agents. The starch granule is deposited in certain cells known as *starch-formers* or *amyloplasts*. It is deposited in these from the periphery to the centre in successive layers. It is carried to the amyloplasts in a soluble and diffusible form by the cell sap, and is there changed into insoluble, indiffusible starch.

**Manufacture.**—Starch may be prepared from the raw materials containing it by either mechanical or chemical methods, or by a combination of the two. Potato starch (*farina*), for example, can be made by grinding the tubers to a pulp and washing out the starch with water. The water containing the suspended starch granules is then strained through a sieve, which allows the granules to pass but retains most of the pulp. The strained mixture is allowed

to stand in settling tanks, when the starch gradually falls to the bottom. The sediment is then washed, and dried at a low temperature. This process is purely mechanical, unless the starch is bleached. In this case either sulphurous acid or potassium permanganate is used. The chemical method of preparing starch consists in treating the raw material with very dilute alkaline solutions, which dissolve proteins and pectins, and saponify fat, thus liberating the starch granules. The latter are then removed by straining or centrifuging, washed, bleached, and dried. Wheat starch is made, also, by a method involving fermentation. The grain is steeped in water till it becomes soft. It is then ground, and again allowed to stand in contact with water till fermentation sets in. As this proceeds, the protein (gluten) is changed gradually into soluble compounds, and the cellular tissue of the grain is disintegrated. The starch granules are thus liberated, and settle down at the bottom of the tank. In another process the dry grain is ground to flour, and made into dough with water. This is washed in a stream of water, which carries away the starch, leaving the gluten behind. In all cases the crude starch thus obtained is rewashed before drying.

**Properties of Starch.**—Pure starch is a white, odourless, tasteless body, insoluble in cold water. If, however, it is ground for some time, particularly in the presence of fine sand, the granules become ruptured, and their contents dissolve gradually when treated with cold water. Air-dry starch contains about 18 per cent. of water, corresponding to the formula  $C_6H_{10}O_5 \cdot 2H_2O$ . This hydrate gives up one molecule of water very readily, forming  $C_6H_{10}O_5 \cdot H_2O$ , and becomes anhydrous at  $100^\circ C$ . Prolonged drying, or treatment with dehydrating agents such as phosphorus pentoxide, changes starch gradually into soluble dextrin. Commercial starches generally contain from 10 to 14 per cent. of water. Starch is a typical colloid. When heated with water, the granules swell up, and become ruptured. If the heating is continued, the starch gelatinizes, forming a colloidal solution or jelly with the hot water, which sets on cooling. The temperature at which this gelatinization occurs varies with different starches. For some common starches these are

Potato	.	.	.	.	.	.	.	65° C.
Wheat	.	.	.	.	.	.	.	72° C.
Maize	.	.	.	.	.	.	.	70° to 74° C.
Tapioca	.	.	.	.	.	.	.	70° C.

When starch paste or jelly is dried, a hard horny mass is obtained, which will not redissolve in water. Not only does the temperature of gelatinization vary with the different starches, but also the nature of the paste. Some take up more water than others, *i.e.* form stiffer pastes or colloidal solutions of greater viscosity. Thus wheat starch gives a thin paste, which has great binding properties. It gives cloth a feeling of increased thickness and the surface a bright appearance and smooth feel. Potato starch produces a much thicker paste but with less binding power, and it gives a dull and roughish surface effect. The temperature at which starch gelatinizes is lowered by the presence of foreign bodies, such as acids, alkalis, and certain salts.

Colloidal solutions of starch differ from those of most colloids in one important particular. As a rule, the viscosity of a colloidal solution increases with keeping, up to a certain maximum. Starch paste or gel, on the contrary, changes gradually on standing into two portions, a liquid containing but little starch and a solid portion containing more starch and less water. There is no increase, but a progressive decrease in viscosity. The initial viscosity of starch solutions of the same concentration compared with water varies with

the nature of the starch. Thus, for solutions containing 12 g. of starch in 30 ml. of water the viscosities are

Potato starch	.	.	.	.	.	.	.	14.3
Cassava	„	.	.	.	.	.	.	4.0
Maize	„	.	.	.	.	.	.	2.5
Wheat	„	.	.	.	.	.	.	1.2
Rice	„	.	.	.	.	.	.	1.0

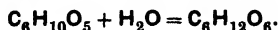
The viscosity of a starch solution determines largely its power of penetrating goods. Those giving solutions with a low viscosity penetrate better than those with a higher viscosity, but the stiffening power varies in the opposite direction.

The *stiffening power* is affected by the completeness with which the starch is gelatinized. If, for any reason, the granules do not burst and gelatinize, loss of stiffening power results. Harrison (*J. Soc. Dyers Col.*, 1911, 27, 84) makes use of this to determine the stiffening power in the following manner: One gram of the starch is suspended in 100 ml. of cold water, and heated with careful stirring to a temperature just above its gelatinizing-point. The mixture is then cooled, and centrifuged in a tube graduated to one-tenth of a millilitre. The ungelatinized granules are thus separated as a deposit, and their volume is inversely proportional to the stiffening power. A commoner method of comparing the stiffening power of starches is the following: A weighed quantity (*e.g.* 5 g.) is made into a cream with a little cold water. This is then stirred into 100 ml. of boiling water, and the mixture is allowed to cool. When it has set, the weight which the paste will carry without breaking the surface is determined. The adhesive power of a paste made from a starch is affected by the moisture it contains. Brown and Heron observed that an ordinary damp starch, when boiled with water, gave an adhesive power which they denoted by the number 1. The same starch after drying at 100° C. had an adhesive value of 2.3, while after drying at 30° C. in a vacuum it rose to 3.28. The same weight of real starch was used throughout. This is of some importance in the selection of starch for dressings. Dry starch is hygroscopic, rapidly absorbing moisture from the air and consequently deteriorating. If dried before use, provided that decomposition has not set in, its stiffening power is increased.

Prolonged boiling of starch with water, or heating under pressure for a shorter time, changes it into a modification known as *soluble starch*, which dissolves, and does not set when cooled. Starch is said to become *thin* when boiled with water, and the longer it is boiled the thinner it becomes.

*Detection*.—Starch is very easily recognized by its power of forming a deep blue-coloured compound with iodine. The nature of a starch can be determined by microscopic examination, each kind of starch having different and characteristic granules. The microscopic structure of the granules of the commoner starches is illustrated in Fig. 163, while Table XLVII gives a summary of their measurements and appearance.

*Action of Acids*.—Concentrated mineral acids dissolve starch at ordinary temperatures. Soluble starch is first produced, but this is quickly changed into dextrose:



Moderately dilute solutions of the acids, when cold, give only soluble starch. Thus, if starch is mixed with a 10 per cent. solution of cold hydrochloric acid and allowed to stand for a few days, it is completely changed into



soluble starch. More dilute acids bring about the same change at the boiling-point, but in this case the reaction proceeds farther, dextrin and dextrose being

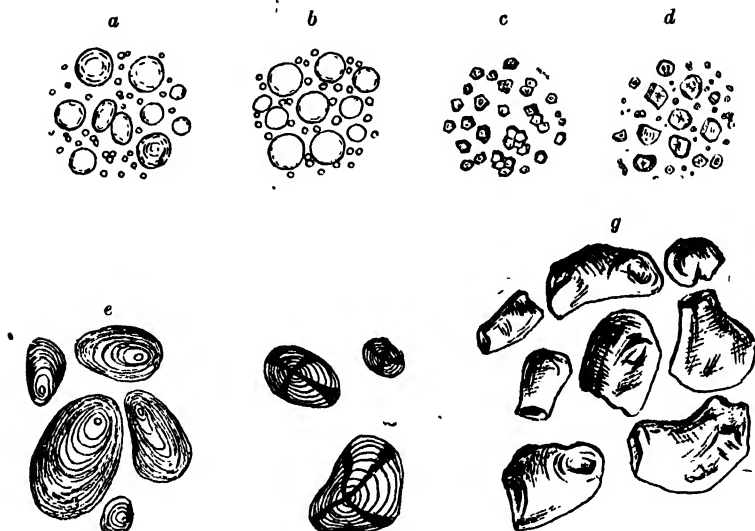


Fig. 163.—Starch Granules from (a) Barley, (b) Wheat, (c) Rice, (d) Maize, (e) Potato, (f) Potato, in Polarized Light,  $\times 300$  (after Stirling); (g) Sagó (after Davies).

also produced. Prolonged boiling causes the starch to become entirely changed into dextrose. Commercial glucose is prepared in this way. Solution of starch is always accompanied by a gradual loss of its colloidal properties and

TABLE XLVII.—VARIETIES OF STARCH.

Name.	Outline.	Measurement.	Surface.	Illum.	Markings.
Potato.	Oval or elliptical.	mm. 1/25 long diam. 1/37 short "	Uniformly but slightly convex.	Dark spot near the narrow end.	Concentric rings closed or almost closed curves.
Rice.	Rectilinear and polygonal.	1/250 . .	Flat . . .	None . .	None.
Maize . .	Rectilinear and polygonal.	1/70 . .	Uneven and slightly concave.	Stellate or irregular, large, central.	None.
Wheat . .	Circular or nearly so.	1/60 . .	Convex . .	Dark spot, eccentric.	Occasionally a few exceedingly faint concentric rings.
Arrowroot (Bermuda)	Oval . .	1/28 long diam. 1/45 short "	Uniformly but slightly convex.	Nearer broad end, circular, crucial transverse line or slit.	Faint concentric rings in a few cases extending about $\frac{1}{2}$ length of grain.
Cassava . .	Rectilinear and polygonal.	1/70 . .	Uneven and slightly concave.	Stellate or irregular, large, central.	None.

the formation of more soluble and diffusible bodies. These, in order of their formation, are

Starch  $\rightarrow$  soluble starch  $\rightarrow$  dextrin  $\rightarrow$  dextrose.

The action is progressive, and all four bodies may exist simultaneously. If the heating is continued beyond the time necessary for the production of

soluble starch, hydrolysis sets in, and the remaining products are formed. The action of acids on starch depends in general upon their dissociation into hydrogen ions, and their rate of action upon the hydrogen-ion concentration or *pH*-value. Salts which hydrolyse in water to give hydrogen ions (*i.e.* acid solutions) act in the same way as acids. Weak acids, including many organic acids, have very little action. But some, such as chloracetic and the naphthalene-sulphonic acids, have a high hydrogen-ion concentration and a correspondingly great hydrolysing action. Acetic and formic acids give rise to esters when heated with starch under pressure. Acetate of starch is the basis of a commercial preparation named *feculose*. The action of acids on starch will be mentioned again under "Soluble Starch" and "Dextrin."

*Action of Alkalis.*—Alkalis have a peculiar action on starch, having an opposite effect to acids. The latter have what is termed a *coagulating action* in inverse proportion to their hydrogen-ion concentration. Alkalis, when they are dissolved in water, give rise to hydroxyl ions, and their action on starch depends upon the hydroxyl-ion concentration. That is, weak alkalis have less action than stronger ones. Salts which produce hydroxyl ions in solution act in a similar manner to alkalis.

The first action of a strong alkali is, in general, to lower the gelatinizing temperature of the starch. If potato starch, for example, is stirred into a cold 1 per cent. solution of sodium hydroxide, it becomes "thick" and swells up gradually into a clear jelly. The rapidity and completeness of the gelatinization are directly proportional to the strength of the alkali used, up to about 2.5 per cent. If excess of the alkaline solution is used, a viscous solution is obtained instead of a jelly. By raising the temperature of the mixture of starch and water, the quantity of alkali necessary to cause gelatinization is proportionately reduced. At temperatures near the gelatinizing-point even traces of alkali have a marked effect. It has been mentioned before that when starch is heated with water, gelatinization is completed only slowly. The addition of a small quantity of alkali causes rapid acceleration and thickening. In fact alkalis are said to *thicken* starch pastes, while acids on the contrary *thin* them. Weak alkalis, such as borax, are commonly used to thicken dressing mixtures. Pastes of great tenacity can be made by gelatinizing starch by means of cold sodium hydroxide solution, and then neutralizing the mixture carefully with a dilute acid. When starch is heated with a solution of sodium hydroxide, it is hydrolysed gradually into soluble starch and dextrin, accompanied by the formation of a brown colour. Much of the colour disappears, however, when the mixture is neutralized with an acid. Potassium hydroxide acts more energetically on starch than the corresponding sodium compound. If, during the action of the alkali, swelling of the granules is prevented, a form of starch is obtained which gelatinizes and forms a paste or viscous solution with cold water. For example, starch is treated with a cold alcoholic solution of potassium hydroxide, and then washed with spirit till free from alkali, and dried at a low temperature. The swelling of starch under the influence of alkalis is prevented also by many salts, such as sodium sulphate or chloride, or a dehydrating agent. A concentrated solution of sodium sulphate may, therefore, be substituted for alcohol in the method described above. Ammonia has no gelatinizing effect on starch, and borax acts only at a high temperature. Calcium and barium hydroxides have a different action. If a saturated aqueous solution of barium hydroxide is added to one containing starch, the latter is completely precipitated owing to the formation of an insoluble addition compound,  $(C_6H_{10}O_5)_4BaO$ . A similar precipitate is obtained with a cane-sugar solution of lime. Since dextrins and gums do not

give any precipitate with barium hydroxide, they may be separated and estimated by means of this reaction. The method is sometimes applicable to the analysis of finishing mixtures.

Starch, after treatment with sodium hydroxide, combines with carbon disulphide in the same way as alkali-cellulose, giving rise to products, similar to viscose, which form viscous, glue-like solutions.

*Action of Formaldehyde.*—Formaldehyde,  $\text{H}\cdot\text{CHO}$ , has a peculiar action on starch, behaving somewhat in the manner of an enzyme. If starch is mixed with a solution of formalin, which is a 40 per cent. aqueous solution of formaldehyde, it gradually becomes changed into an opalescent liquid at ordinary atmospheric temperatures. This is due to the fact that the presence of formaldehyde causes a reduction in the temperature of gelatinization. Even dilute solutions of the reagent will bring about this change, but the reaction is slower. The presence of acid seems also to assist, as, if the formaldehyde is neutralized, its action becomes much slower. The liquefied starch no longer gives a blue colour with iodine solution. On this account it was thought that the action of the formaldehyde resembled that of diastase, and that the starch was hydrolysed to simpler compounds. Probably, however, this view is not correct. It is more likely that loosely-combined addition compounds are formed, since the starch can be reproduced by the addition of alcohol and certain salts such as ammonium acetate. Other modifications of starch are obtained by the action of formaldehyde under varying conditions, some of which may have uses in textile trades. Thus, an insoluble and non-gelatinizing product is obtained by heating starch with an aqueous solution of formaldehyde and a sufficient quantity of an ammonium salt to form hexamethylene-tetramine,  $(\text{CH}_2)_6\text{N}_4$ , at a temperature below its gelatinizing-point.

*Action of Salts.*—From what has been said above, it will be seen that, in general, the action of salts on starch depends upon whether hydrogen or hydroxyl ions predominate in their solutions. Acid salts act just like acids. Those which hydrolyse in solution, like magnesium chloride, also act in the same way. Salts which give alkaline solutions, such as potassium sulphocyanide, gelatinize starch in the cold like an alkali. All of these are used in making starch pastes or adhesive preparations. For example, a well-known office paste is made by heating starch and water with magnesium chloride. Zinc chloride is often used for the same purpose. Deliquescents like zinc and magnesium chloride also keep the paste from becoming too brittle when dry, and this makes it more suitable for such things as labels. Concentrated solutions of certain salts, e.g. calcium nitrate, calcium chloride, calcium sulphocyanide, and zinc chloride, dissolve starch when cold.

*Action of Micro-organisms and Enzymes.*—Starch is readily attacked by bacteria, moulds, yeasts, and enzymes. This action is accompanied generally by the production of soluble starch, dextrin, or dextrose, together with other products, such as acids. Damp starch becomes acid in reaction owing to the growth of the acid-forming organism, and boils "thin" in consequence. *Bacillus subtilis* causes the gradual liquefaction of starch, with the production of soluble starch and dextrin. *Aspergillus oryzae* is particularly active, converting the starch at  $38^\circ \text{C}$ . very quickly into dextrin and dextrose. This is due to the presence of an enzyme, known as *taka-diastase*. Similar enzymes contained in saliva, the stomach and pancreas of animals, act in the same way. Their use for this purpose in cotton-bleaching has been mentioned, and the action of diastase has been described in Chapter IV.

**Soluble starch** may be prepared in many ways. In solution it is obtained by the prolonged boiling of starch with water, or, more rapidly, by the addition

of a small quantity of a hydrolysing agent, such as an acid or an alkali, or of an oxidizing agent. The limited action of diastase may also be made use of. But, since some dextrin and dextrose will be simultaneously formed, solutions of soluble starch prepared by these methods contain these bodies also. Pure soluble starch may be made by soaking potato or other starch in a cold 10 per cent. solution of hydrochloric or sulphuric acid for some days, or until a sample, after washing, dissolves completely in boiling water and does not gelatinize when cooled. When this point is reached, the starch is washed, by sedimentation, with cold water till free from acid, and is then slowly dried in a stream of warm air. A readily soluble product, but accompanied by some dextrin, is made by moistening starch with a dilute solution of an acid, and drying the mixture slowly at a low temperature. For example, potato starch is moistened with a 0.1 per cent. solution of nitric acid, and dried at 40° C. Solutions of soluble starch may be prepared also by heating starch with water containing small quantities of oxidizing agents, such as sodium hypochlorite or perborate, either alone or in the presence of acid.

Dry soluble starch is insoluble in cold water. The granules are not ruptured but only modified. The origin of the starch can still be determined by microscopic examination. When it is mixed with boiling water it dissolves, forming a clear or opalescent solution, and not a jelly or paste like ordinary starch. This solution does not set, but remains liquid on cooling, unless unchanged starch is present. But the cold aqueous solution, on standing, forms gradually a precipitate of insoluble starch. Soluble starch has comparatively little adhesive power, but it naturally penetrates goods better than starch pastes. It is suitable for use only where penetration is required and the surface is uncovered. It is used also for thinning-down thick starch preparations. But in such cases a so-called "thin starch" would be used, or a preparation of ordinary starch thinned by boiling or by means of diastase.

**Thin starches** are mixtures of ordinary starch with soluble starch and dextrin, made by moistening starch with acid and drying it carefully. The composition of the product depends upon the nature and quantity of acid used and the temperature of drying. These starches are naturally acid, and contain also some dextrose, as is seen from the analyses in Table XLVIII.

TABLE XLVIII.—COMPOSITION OF THIN STARCHES.

	1.	2.
Water . . . .	8.00	10.40
Mineral matter . . . .	0.05	0.00
Dextrin . . . .	22.86	20.25
Dextrose . . . .	7.03	6.95
Starch . . . .	62.06	62.40

Starch containing dextrose is liable to become sour, since dextrose favours the growth of micro-organisms. Further, goods dressed with starch containing dextrose, especially in the presence of acid, often become discoloured on keeping, owing to the formation of caramel.

**Dextrin**,  $(C_6H_{10}O_5)_n$ , is a product intermediate between starch and sugar. It can be made from starch by the following methods: (i) When starch is dehydrated, especially with the aid of powerful dehydrating agents, such as phosphorus pentoxide, it is gradually transformed into dextrin. (ii) Starch

mixed with water and heated under pressure to a temperature of about 240° C. gives a soluble dextrin. (iii) When dried and heated to a temperature of 210° C., starch is slowly changed into dextrin, accompanied by the production of a brownish colour. (iv) Mixed with small quantities of acids, such as nitric, hydrochloric, or lactic acid, this change takes place more quickly and at a lower temperature. Thus, if farina is moistened with a 1 per cent. solution of nitric acid and slowly dried at a temperature of 50° C., it is changed into soluble dextrin. (v) Starch is converted by diastase into a mixture of maltose and dextrin. The proportion of dextrin produced depends upon the quantity of the ferment present and on the temperature of the reaction. By controlling these, a product rich in dextrin may be obtained (Chapter. IV). (vi) Certain bacteria, such as *Bacillus macerans*, in the presence of small quantities of nitrogenous and saline foods, convert starch into dextrin. (vii) Solutions of dextrans, containing very little sugar, are produced when starch and water are heated under pressure to about 240° C. with traces of acids.

In practically all of the above methods of preparation the starch is first changed into soluble starch, then into dextrin, and finally, if the reaction is continued long enough, the dextrin is converted into sugar. Commercial dextrin, therefore, is not a single substance, but a mixture of variable quantities of starch, soluble starch, dextrin, and sugar, together with, in many cases, the acid used in the conversion. As a general rule, light-coloured dextrans contain much soluble, and often some unchanged, starch, while dark-coloured dextrans contain mostly dextrin and sugar. For use in finishing, colourless solutions of dextrans containing comparatively little starch or sugar may be prepared by heating a mixture of starch and water to 70° C., and then adding about 2 to 3 per cent. of diastase or a similar preparation. The mixture is constantly stirred and kept at 70° C. till it no longer gives a blue colour with iodine solution. A little alkali is then added, or the temperature raised quickly to 100° C., to inactivate the diastase and complete solution.

There are several different forms of dextrin, which may be distinguished roughly by their reaction with iodine solution. For commercial purposes the dextrans may be divided into the following groups:—

(1) *Amylodextrans*.—These are only slightly soluble in cold, but readily soluble in hot, water. They do not reduce Fehling's solution, and give a blue colour with iodine solution. They are the principal constituents of soluble starch. Amylodextrans are insoluble in 40 per cent. alcohol.

(2) *Erythrodeoxtrans*.—These dextrans are readily soluble in water, and are insoluble in 50 per cent. alcohol. They give a red or reddish-brown colour with iodine solution.

(3) *Achrodeoxtrans*.—These are soluble in water but insoluble in 70 per cent. alcohol. They give no colour with iodine solution. British gum, gommeline, starch gum, and similar preparations all consist chiefly of these dextrans.

Dextrin is a white, amorphous, solid substance, with neither taste nor smell. It is deliquescent and soluble in cold water. Its solution is highly dextrorotatory, having a value  $[\alpha]_D = +186^\circ$ . Dextrin is precipitated from its aqueous solution by adding alcohol or a freshly-prepared solution of ammoniacal lead acetate. The latter is prepared by mixing 100 ml. of saturated lead acetate solution with 26 ml. water and 8 ml. strong ammonia solution. When boiled with dilute acids for about three hours, dextrin is changed completely into dextrose. It has no reducing action on Fehling's solution, and is not changed by fermentation with yeast. Practically all commercial dextrans reduce Fehling's solution, but this is due to the presence of dextrose. Dextrin may be distinguished from gums, such as gum-arabic, by the fact that it gives

no precipitate with a neutral alcoholic solution of ferric chloride. To prepare neutral ferric chloride solution, some of the ordinary solution is boiled with a little ammonium carbonate and filtered. One gram of the dextrin is then dissolved in about 30 ml. of the distilled water, and mixed with an equal volume of 56 per cent. alcohol. A trace of precipitated chalk is then added, together with a few drops of the ferric chloride solution. In the presence of gum a brownish precipitate is produced.

**Commercial Dextrin.**—There are two varieties of commercial dextrin, viz. yellow and white. The latter consists chiefly of soluble starch, and is made by methods similar to those employed for the preparation of thin starches. In yellow dextrins the process has been carried further, and the starch is more completely changed. During dextrinization some dextrose is always produced; yellow dextrins may contain considerable quantities. The difference between the two kinds is seen in the analyses given in Table XLIX.

TABLE XLIX.—COMPOSITION OF YELLOW AND WHITE DEXTRIN.

	White Potato Dextrin.	Yellow Potato Dextrin.
Water . . . .	12.86	12.58
Mineral matter . . . .	0.41	0.36
Dextrin . . . .	29.00	83.11
Dextrose . . . .	1.20	3.73
Soluble starch . . . .	56.53	0.22

Yellow dextrin, unless it contains unchanged starch, dissolves in cold water; white dextrin is only partly soluble, its solubility being determined by the amount of dextrin it contains. It is completely soluble in boiling water. The solution should not form a jelly on cooling. If it does, the presence of unchanged starch is indicated. Dextrin gives a very soft, full finish to goods, but has little stiffening power compared with starch.

**Gelatin and Glue.**—These substances are used to a limited extent when a hard stiff finish is required, or in such goods as veilings and nets, where the threads require considerable support without any appreciable filling, but starch is cheaper and is used when possible. Both glue and gelatin are made from the same materials, viz. skin, horn, and bone, the difference between them being due only to the care exercised in the selection of the raw materials and in manufacture. Gelatin is, in fact, simply purified glue. Neither bones nor skin contain gelatin but a substance which can be converted into it by hydrolysis on boiling with water. This glue-forming substance is termed *ossein* or *collagen*, according to whether it is derived from bones or skin.

In the manufacture of gelatin, the raw materials are first freed from impurities by washing or other means. They are then heated with water to obtain a dilute solution of gelatin. This is clarified by filtration, concentrated, bleached, and allowed to set. The jelly is then cut into cakes, and dried in a current of warm air.

In the case of bones, the process is somewhat complicated. If glue is required, they are degreased with benzene, and then heated under pressure with water to extract the glue. The residual calcium phosphate is used as manure or is calcined into bone-ash. If it is desired to make gelatin, the degreased bones are thoroughly cleansed, and soaked in dilute mineral acid (generally hydrochloric) to dissolve calcium phosphate. This is then washed away with water, leaving a horny residue of ossein. The ossein, after washing

and neutralizing with lime-water, is heated with water at about 80° C., when it dissolves, giving a solution of gelatin. For skin, in the case of both glue and gelatin, the process is simpler. Tanner's waste pieces, which have been soaked in milk of lime, are first delimed by washing with water, treating with dilute acid, and again washing. The delimed pieces are then heated with water at a temperature of from 70° to 80° C. The fat is skimmed off as it rises to the surface, and the dilute solution of gelatin is drawn off, clarified, evaporated, bleached, and dried. Both gelatin and glue are made at the same time, the first liquors giving gelatin, and the later ones glue. The purity and value of the final products depend not only upon the careful selection and purification of the raw materials, but also largely upon the care taken during manufacture to avoid undue hydrolysis. If the heating is too prolonged, or the temperature too high, or even if traces of acids or alkalis are present during the extraction, the hydrolysis does not stop at the formation of glutin. This body also is decomposed by hydrolysis, with the formation of soluble non-colloidal compounds termed *peptones*, while still more prolonged heating causes these peptones to break down into still simpler bodies, such as glycine,  $\text{CH}_2(\text{NH}_2)\cdot\text{COOH}$ , and leucine,  $(\text{CH}_3)_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{COOH}$ .

These amino acids and peptones are produced also under favourable conditions by the action of putrefactive bacteria on the raw materials, the liquors, or the drying jelly. Glue and gelatin differ chiefly in the proportions of these hydrolysed products which they contain. This may be seen in the analyses given in Table L. Peptones not only have no gelatinizing or stiffening power, but are also very hygroscopic. Goods dressed with the bad glue in the Table would have a damp feel. They would probably become mouldy or would be attacked by bacteria. Peptone is an ideal food for bacteria, and the dampness of the goods would encourage their development.

TABLE L.—COMPOSITION OF GELATIN AND GLUE.

	Gelatin.	Good Glue.	Bad Glue.
Water . . . . .	14.00	14.23	16.23
Mineral matter . . . . .	1.58	1.33	2.75
Glutin . . . . .	80.00	78.08	64.35
Peptones and other nitrogen compounds	0.50	1.95	11.10
Non-gelatinous bodies, by difference .	3.92	4.41	5.57

Glue and gelatin are typical colloids. They dissolve only in hot water, and their solutions set to a jelly when cooled. In order to make a solution of glue, the cakes should be soaked for some hours in cold water. A good sample will take up five times its volume of cold water and should form a firm jelly, leaving the excess of water nearly colourless. If a soft or sticky jelly is formed, and much colour is found in the water, the sample is of low grade and is unsuitable for textile use. The water is poured off, and the swollen glue is placed in fresh water and warmed gently to about 30° C., at which temperature it dissolves readily. Overheating of glue or gelatin solutions should always be avoided, since it causes hydrolysis and diminishes the stiffening power.

Glue and gelatin form insoluble compounds with formaldehyde, which are made use of in the production of waterproof dressings. These may be obtained by treating the goods with a gelatin solution and, after drying, either subjecting

them to the action of formaldehyde vapour or passing them through a cold dilute solution of formaldehyde in water. Small quantities of potassium dichromate, after exposure to light for some time, also render gelatin insoluble in water. An aqueous solution of gelatin gives a whitish precipitate with tannic acid. The reaction is very delicate, being capable of detecting one part of gelatin in 5000 of water if excess of tannic acid is present. Since mineral acids interfere with the reaction, it is best to use a solution of tannic acid containing sodium acetate. Another very delicate reaction is the formation of insoluble chloramines (or bromamines) with either chlorine, bromine, or acidified bleaching-powder solution. When a saturated solution of picric acid is added to a cold aqueous solution of gelatin, a precipitate is produced, which at first dissolves, but becomes permanent in the presence of excess of the reagent. This reaction serves also for the detection of gelatin. These reactions do not, however, distinguish it from proteins; but, unlike proteins, gelatin solutions give no precipitate with copper sulphate solution, nor with potassium ferrocyanide in neutral solution or in one made faintly acid with acetic acid.

*Analysis of Glue and Gelatin.*—For textile purposes the most important tests are (i) the weight of water absorbed, and (ii) the nature and strength of the jelly formed.

*Water absorbed.* A small piece of the sample, weighing from 3 to 5 g., is suspended in a beaker of cold water by means of a silk thread for forty-eight hours. At the end of this time it is removed, and the excess of water carefully removed with filter-paper. The jelly is then weighed. From the increase in weight the percentage of water absorbed can be calculated. The appearance of the jelly is also noted as described above.

*Strength of jelly, or consistency.* Five grams of gelatin or 10 g. of glue is soaked overnight in 100 ml. of cold water in a small beaker or pot. The vessel is then heated in warm water till the jelly has dissolved. After mixing, the solution is covered, and allowed to stand for some hours to set.

A sinker (Fig. 164) is then placed on the jelly so that the portion *CBD* rests vertically on the surface. The weight of the apparatus is known. Its measurements are conveniently  $CD = \frac{1}{2}$  in.;  $BC = 1$  in.;  $AB = 9$  in. Small shot is poured carefully into the cup till the pointed end of the sinker just breaks the surface of the jelly. The shot required is then weighed, and the result, added to the weight of the sinker, gives the weight which is necessary to break the jelly.

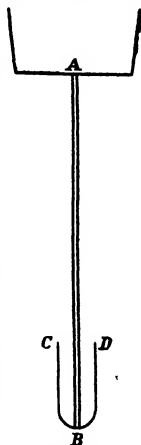


Fig. 164.

Good results are obtained also by the *finger test*. Ten grams of the glue is dissolved in 100 ml. of water, and allowed to set in a cylindrical pot. In a number of exactly similar pots, varying weights of a standard glue or gelatin are dissolved in 100 ml. of water, and allowed to set side by side with the glue. When these have all set, the strength of the glue jelly which is under test is matched against them by lightly pressing the surface with the finger-tips, and that particular strength of gelatin noted which offers the same resistance to the finger as the glue. The strength of the jelly is then expressed as a percentage of the standard used. For instance, 10 g. of glue gave a jelly equal in consistency to that obtained from 3.5 g. of gelatin. Hence the consistency of the glue is said to be 35.

*Algin* occurs in various seaweeds, particularly in *Laminaria digitata*. When this seaweed is boiled for some time with water or a dilute solution of sodium carbonate, the algin is dissolved, forming a viscous solution. If this



solution is acidified, insoluble white alginic acid is formed. With solutions of many metallic salts, such as calcium chloride or zinc sulphate, insoluble metallic alginates are produced. These reactions are sometimes made use of in dressing cotton goods. Algin is met with either as a dried horn-like mass or as a mucilage. The latter contains from 5 to 10 per cent. of alginic acid. Algin contains nitrogen, and, in some respects, is similar to a solution of a protein, but it does not give a precipitate with tannic acid or mercuric chloride.

**Gum-tragacanth** is a dried exudation derived from the *Astragalus gummifer* tree, which grows in Central Asia and South America. It occurs in either small, whitish, flat chips, cylindrical sticks, or powder form. When boiled for some hours with water, it gives up about 60 per cent. of its weight. When soaked in cold water, it swells up and forms gradually a thick jelly, which becomes liquid on warming, setting again when cooled. The solution has a very high viscosity, which is greater than that of gum-arabic. The jelly is not clear, but contains opaque specks, consisting of tissue containing starch granules rather similar to those of maize. Gum-tragacanth is too expensive for general use.

**Gum-tragacal** is obtained from the twist bean, the fruit of a tree, by extraction with hot water. It forms a jelly similar to that given by gum-tragacanth. It contains no starch, but some nitrogenous constituents are present. It has considerable binding properties, and imparts a soft leathery feel.

**Gum-arabic** is the dried exudation of trees of the acacia species, growing chiefly in the Sudan. Its chief constituent is arabic acid, which is present as a calcium salt. The gum is completely soluble in water, and gives a highly viscous and adhesive solution. The adhesive properties are increased by the addition of a little alum to the solution, which gives a mixture of the aluminium and calcium salts of arabic acid. A solution of gum-arabic gives precipitates with borax, mercuric chloride, and ferric chloride, and it is thrown down unchanged by alcohol.

**Irish moss** is a variety of seaweed. When heated with water, a thick solution is formed. If this is strained and allowed to cool, a jelly is obtained which consists chiefly of pectins.

**Pectic acid** is precipitated from solutions of Irish moss by the addition of a mineral acid. It produces a soft finish, useful for lightly-dressed goods requiring a so-called natural finish. It is said to prevent the bleeding of dye-stuffs during washing. The moss is steeped in cold water for twelve hours, and then boiled for two, and strained. A preservative must be added to the preparation. An average commercial sample contains

Water	.	.	.	.	.	13 per cent.
Soluble matter	.	.	.	.	.	45 "
Mineral	"	.	.	.	.	2 "
Insoluble	"	.	.	.	.	40 "

**Iceland moss** is a variety of lichen. It is much cleaner than Irish moss, and contains nearly 70 per cent. of soluble matter, which is chiefly pectin. It is used in the same way as Irish moss.

**Carnaúba wax** is an exudation obtained from the leaves of a South American palm. It is a whitish, hard, brittle substance, with a high melting-point, 80° to 84° C. If melted in water containing a little sodium carbonate or borax, an emulsion can be prepared which has marked stiffening power. The wax can be saponified by prolonged boiling with sodium-hydroxide. From the solution of the sodium soap thus obtained an insoluble zinc soap may be precipitated which is fairly soluble in benzene and does not decompose on storing.

## Filling Materials.

**Kaolin, or China-clay**, is a hydrated silicate of aluminium found chiefly in Cornwall. Its composition is approximately  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ . It is a white amorphous powder having a specific gravity of 2.2. Table LI, taken from Hurst (*Dictionary of Chemicals and Raw Products*), gives its average composition.

TABLE LI.—COMPOSITION OF CHINA-CLAY.

	Cornwall.	China.	French.
Silica, $\text{SiO}_2$ . . . . .	46.78	51.50	48.37
Alumina, $\text{Al}_2\text{O}_3$ . . . . .	39.60	33.76	34.95
Water . . . . .	13.16	10.24	12.00
Potash, $\text{K}_2\text{O}$ . . . . .	0.12	1.90	1.26
Ferrio oxide, $\text{Fe}_2\text{O}_3$ . . . . .	0.09	1.80	1.26
Lime, $\text{CaO}$ . . . . .	0.07	..	..
Magnesia, $\text{MgO}$ . . . . .	..	0.80	..

**Talc**, sometimes termed **French chalk**, is a hydrated silicate of magnesium of the formula  $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ . It is a translucent mineral, having a specific gravity of 2.5 to 2.8. When ground it has a soft, soapy feel. The chief impurities are clay, calcium, and iron compounds. Good talc contains at least 98 per cent. of matter insoluble in hydrochloric acid.

**Calcium sulphate** occurs native as anhydrite,  $\text{CaSO}_4$ , and as gypsum, satin-spar, alabaster, selenite, and other varieties having the formula  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . It is obtained also as a by-product in certain manufacturing processes. Gypsum is a white powder, which, when dried at  $110^\circ$  to  $120^\circ \text{C}$ ., loses one molecule of water, forming plaster of Paris,  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ . At  $200^\circ \text{C}$ . it becomes anhydrous calcium sulphate,  $\text{CaSO}_4$ . Low-grade samples may contain iron oxide, and magnesium and calcium carbonates. Examples of commercial samples of ground and burnt gypsum are given in Table LII.

TABLE LII.—COMPOSITION OF COMMERCIAL SAMPLES OF GYPSUM.

	(1) Raw.	(2) Raw.	(3) Burnt.	(4) Burnt.
Silica . . . . .	4.41	0.98	1.54	0.12
Iron oxide and alumina . . . . .	1.15	..	2.20	0.52
Calcium sulphate . . . . .	70.79	79.66	86.88	98.96
Magnesium sulphate . . . . .	0.52	..	..	..
Calcium carbonate . . . . .	3.32	..	..	..
Magnesium carbonate . . . . .	3.60	..	..	..
Water . . . . .	16.21	19.36	9.38	0.40

**Barium sulphate**,  $\text{BaSO}_4$ , occurs native as barytes. It is a white substance with a specific gravity of 4.6. It is completely insoluble in either water or acids. Precipitated barium sulphate is obtained in manufacturing processes when barium carbonate is used to neutralize sulphuric acid:



It is generally sold as a paste containing about 30 per cent. of water. Barium sulphate has little covering power, though, naturally, great weight-giving properties.

**Magnesium sulphate (Epsom salts),  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ .**—This body is used both as a weighting material and also as a deliquescent agent. It occurs native as kieserite,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ . When this mineral is treated with water, the magnesium sulphate is dissolved, and may be removed from the accompanying impurities by filtering the solution. When this is concentrated, colourless crystals of Epsom salts are obtained. These are readily soluble in water. They form double salts with the sulphates of the alkali metals, e.g.  $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ . When crystalline magnesium sulphate is heated, it loses its water of crystallization, becoming opaque and crumbling to a powder. At  $100^\circ \text{C}$ . it is changed into  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ , becoming anhydrous at  $200^\circ \text{C}$ . The dehydrated forms, when exposed to the air, attract atmospheric moisture, and become again hydrated. Thus, when goods are dressed with Epsom salts and dried, they either retain the water of crystallization or take up moisture according to the temperature at which they were dried.

**Sodium sulphate (Glauber's salt),  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,** is, like Epsom salts, both a filling and a deliquescent agent. It is found native as anhydrous sulphate and also in combination with calcium sulphate as glauberite,  $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$ . It is also prepared during the manufacture of alkali by the Leblanc process. It crystallizes from water in the form of colourless prisms of the composition  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . When exposed to air, these crystals effloresce and become  $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . The tenth molecule of water is given off at  $100^\circ \text{C}$ . Anhydrous sodium sulphate attracts moisture from the air as does magnesium sulphate.

### Softening Agents.

**Soap** is very commonly used as a softening agent. **Turkey-red oil** is useful, and **glycerin**, in small quantities, gives excellent results. If, however, much glycerin is used, goods become damp owing to its hygroscopic properties. Other softening agents are—

**Petroleum Jelly.**—This is a mixture of paraffin wax with petroleum. It has, as a rule, a melting-point of about  $40^\circ \text{C}$ .

**Ceresine** is a wax obtained from a bituminous mineral named *ozokerite*. Its melting-point is  $60^\circ$  to  $70^\circ \text{C}$ .

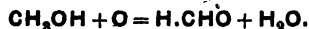
**Japan wax** is a yellowish wax obtained from the berries of a Japanese plant. It melts at  $50^\circ \text{C}$ . When shaken with hot water, it forms fairly stable emulsions; this property enables it to be mixed readily with finishing preparations.

**Tallow** is prepared from beef and mutton fat. It is a white, tasteless substance. When carelessly prepared; or after prolonged keeping, it becomes rancid, free fatty acids being liberated.

**Proprietary Softening Mixtures.**—These are very numerous, and consist generally of mixtures of soap and oils in varying proportions.

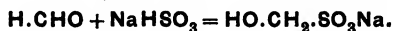
### Antiseptics.

**Formaldehyde,  $\text{H} \cdot \text{CHO}$ ,** is made by the oxidation of methyl alcohol,  $\text{CH}_3\text{OH}$ :



It is a gas with a powerful, penetrating smell, dissolving readily in water, giving commercial *formalin*, which contains about 40 per cent. of dissolved

formaldehyde. When this aqueous solution is kept for a long time, or is evaporated over sulphuric acid, the aldehyde is polymerized, and crystals of *paraformaldehyde*,  $(\text{CH}_2\text{O})_n$ , are obtained. Formaldehyde is a very powerful antiseptic, but since it is volatile it is not suitable for finishing mixtures. It reacts with ammonia, forming *hexamethylene-tetramine*, *hexamine*,  $(\text{CH}_2)_6\text{N}_4$ . It reacts in a similar manner with proteins, gelatin, and other bodies containing an amino group. It combines also with bisulphites, giving bodies similar to decrolein:



Formaldehyde is used in dyeing for certain purposes. The strength of a commercial solution of formaldehyde (formalin) may be ascertained approximately from its specific gravity and reference to Table LIII.

TABLE LIII.—SPECIFIC GRAVITY OF FORMALDEHYDE SOLUTIONS.

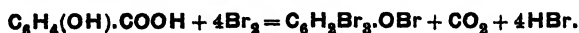
Specific Gravity at 15.5° C.	Percentage of Formaldehyde by Weight.	Percentage of Formaldehyde by Volume.
1.0025	1.0	1.0
1.0125	5.0	5.0
1.0250	10.0	10.25
1.0380	15.0	15.60
1.0530	20.0	21.1
1.0670	25.0	26.7
1.0830	30.0	32.5
1.1040	35.0	38.6
1.1250	40.0	45.0

**Boric acid**,  $\text{H}_3\text{BO}_3$ , occurs in natural jets of steam (*suffioni*), which escape from the earth in certain volcanic districts, notably in Tuscany. The condensed steam collects in pools, and is concentrated till the acid crystallizes out. It is a white lustrous substance with a soapy feel. It is not very soluble in water: at 100° C. 100 parts of water dissolve 27.5 of boric acid, and at 0° C. 1.95. It is volatile in the presence of steam. When it is neutralized with sodium hydroxide, and the resulting solution is crystallized, **borax**,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , is obtained. Both boric acid and borax are used as preservatives, but they are not very powerful in their action, from 1 to 3 per cent. being necessary.

Boric acid may be detected by its property of giving a pink colour with turmeric. In a fabric or dressing mixture the test would be performed as follows: A portion of the sample is made alkaline with sodium hydroxide, and completely charred in a platinum dish. The char is extracted with dilute hydrochloric acid. A turmeric paper is then soaked in the solution, and dried on a glass plate placed on the water-bath. In the presence of boric acid the paper becomes pink, the colour changing to blue or violet when moistened with ammonia solution.

**Salicylic acid**,  $\text{C}_6\text{H}_4(\text{OH}).\text{COOH}$ , is a colourless crystalline compound with a sweetish taste. It melts at 156.75° C. It is only sparingly soluble in water, one part of the acid requiring 550 of water at ordinary temperatures. It volatilizes with the steam when its aqueous solution is boiled. When neutralized with alkalis, it gives rise to salts termed *salicylates*. When a

neutral solution is treated with excess of bromine-water, a pale yellow insoluble precipitate is produced:



When ferric chloride or other soluble ferric salt is added to a solution containing salicylic acid, a deep violet coloration is obtained. This reaction makes freedom from iron essential in mixtures in which salicylic acid is used. Not less than 0.5 per cent. is required.

**Zinc chloride**,  $\text{ZnCl}_2$ , crystallizes from water in the form of colourless crystals of the composition  $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$ . Dry zinc chloride is very deliquescent, and it is used both as a deliquescent and as a preservative for size. For the latter purpose from 5 to 6 per cent. is necessary. It dissociates when heated, giving hydrochloric acid. This is a frequent cause of tendering in cotton goods when the yarn from which they are made has been sized with starch and zinc chloride. But zinc chloride is very commonly employed in the preparation of sizing mixtures, since it also assists in the gelatinization of the starch.

### Blueing Materials.

The chief of these are coal-tar dyes, indigo, ultramarine, and smalt.

**Ultramarine** is a mixture of silicates of aluminium and sodium with sodium polysulphide, made by igniting a mixture of china-clay, silica, sodium hydroxide, sodium sulphate, and rosin. It is rarely adulterated, but the colouring power depends upon the formula used in manufacture and the fineness of the powder. This can be tested by diluting it with a white powder such as kaolin, until it has the same tint as a given quantity of a standard compound, or by diluting the standard in the same way to match the powder. When treated with chlorine, ultramarine becomes red. Its colour is destroyed also by dilute acids, with the evolution of sulphuretted hydrogen. Thus, when it is used as a blueing agent, goods should be quite free from chlorine and acid.

**Smalt** is essentially glass coloured with cobalt oxide, and is made by fusing a mixture of silica, potassium hydroxide, and oxide of cobalt. It is tested like ultramarine. It is not changed by either chlorine, acids, or alkalis.

### Fireproofing Agents.

The following are the chief compounds used for this purpose: (i) metallic oxides, such as tin oxide or alumina; (ii) compounds of ammonia, such as the chloride or phosphate; (iii) sodium phosphate, borate, silicate, stannate, or tungstate; (iv) alum.

These bodies are either mixed with the dressing mixture or produced on the goods by double decomposition. Thus, cotton may be soaked in a solution of alum and then passed through a bath of a dilute alkali, or alternate baths of magnesium and sodium phosphate may be used. The method adopted depends upon whether or not the goods must stand washing. Flannelette is treated by Perkin's method. It is first impregnated with a solution of sodium stannate,  $\text{Na}_2\text{SnO}_3$ , squeezed, and dried, and then worked in a bath of ammonium sulphate. It is then washed and dried. This process leaves tin oxide deposited in the fibre, and it is retained so firmly that it cannot be removed by washing.

Temporary fireproofing of cotton goods may be produced by soaking them in a 10 per cent. solution of almost any of the soluble salts mentioned above. Ammonium phosphate or sulphate and alum are commonly used. In the

case of ammonium sulphate a little borax should be included in the mixture, otherwise the goods may become tendered owing to the gradual liberation of sulphuric acid.

**Sodium tungstate**,  $\text{Na}_2\text{WO}_4$ , is one of the most efficient of fireproofing agents, but is rather too expensive for general use.

**Preparation of Finishing Mixtures.**—The starch is weighed out, ground into a cream with cold water, and passed through a sieve into a tub. This is made of wood or copper, and has a capacity of about 50 gallons. A copper steam-pipe is provided, which discharges through a spreading nozzle at the bottom of the tub. Sufficient water is placed in the tub to make, together with the condensed steam, the required volume of finishing mixture. The contents of the tub are heated gradually by steam till the starch gelatinizes, and the other ingredients are then added and stirred in thoroughly. The heating is continued till the proper consistency is reached. Kaolin and other insoluble filling materials are ground in a mill before use.

**Application of the Finishing Mixture.**—The mixture is applied by means of a mangle. The type of mangle used depends upon the finish required. The chief kinds are:—

- (1) Simple stiffening mangles.
- (2) Friction mangles.
- (3) Back-filling mangles.
- (4) Back-starching or skimming mangles.

A common form of simple stiffening mangle is shown in Fig. 165, made by Messrs. Whitehead & Poole. The two bowls are made of wood. The lower dips into the starch box, and gathers up and applies the mixture, while the nip ensures its even distribution. The starch box contains also a guide roller, round which the cloth is sometimes passed through the starch on its way to the nip.

Friction mangles are used when it is necessary to fill the cloth with the maximum quantity of material that is possible, and the goods are passed two or more times through the mixture. In Edmeston's friction mangle a lower cotton bowl gathers up the filling mixture and applies it to the goods. The upper bowl, which consists of wood, revolves at a slightly greater speed than the lower one, and the friction thus produced forces the filling mixture into the cloth.

In the back-filling mangle, the cloth can be passed through the starch box with one face applied closely to the bowl, so that it is starched on only one side. A type of these mangles, made by Messrs. A. Edmeston & Sons, Ltd., is shown in Fig. 166. A revolving agitator ensures the regular application of the starch to the exposed face of the cloth. A rubber scraper or *doctor*, *R*, scrapes the bowl, so that it always presents a clean surface to the incoming cloth. On the opposite side a similar metal doctor *M* removes excess of starch, and ensures the uniform distribution of the filling.

In skimming or back-starching mangles, the starch is pasted on to the lower surface of the cloth as it passes horizontally through the machine. The method is illustrated by Fig. 167. The cloth is threaded over guide winces, and passed horizontally over the starch box. The larger roller gathers up and applies the mixture to the cloth, the smaller acting as a doctor and regulating the feed of the starch according to the space between the two.

After starching, the goods may be finished by means of the mechanical methods described already. But they are subjected sometimes also to special

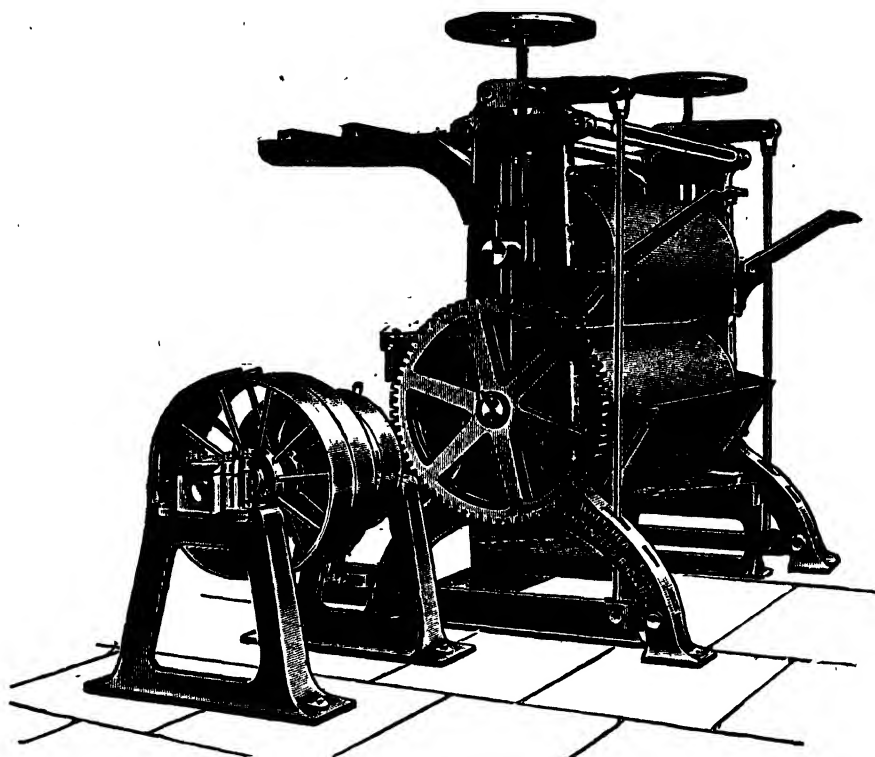


Fig. 165.—Two-bowl Starch Mangle.

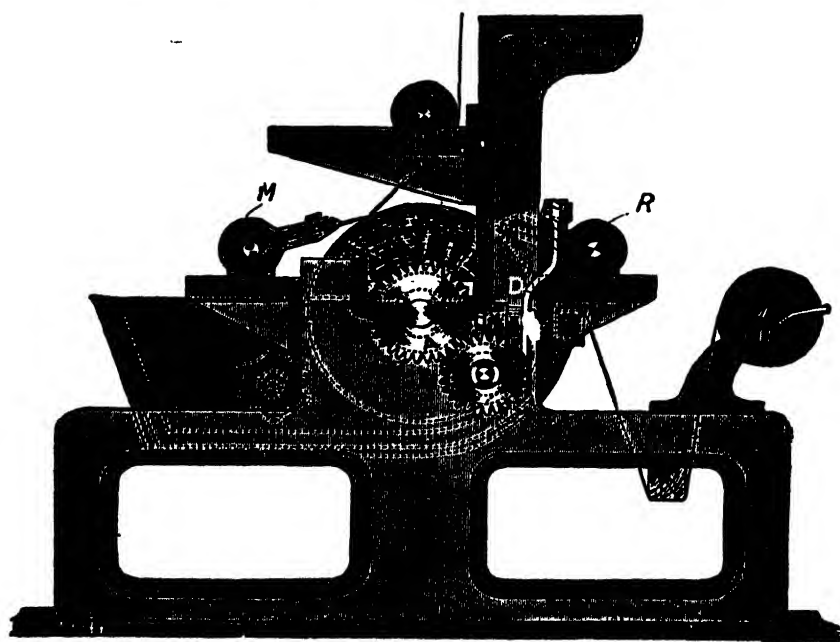


Fig. 166.—Edmeston's Back-filling Mangle (Side View).

processes to alter the feel of the cloth or to break down the harshness of the finish. Light goods are commonly *stentered*.

**Stentering.**—The effects produced by this process include: (i) recovery of width; (ii) straightening of threads or pattern; (iii) drying with warm air

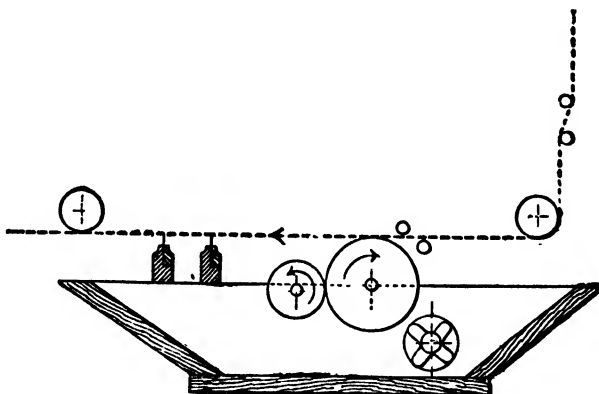


Fig. 167.—Back-starching Machine.

while in the straightened-out condition; (iv) producing the desired feel by controlling the rate of drying, and applying at the same time a special motion termed *swissing*. These processes are used very commonly for lace goods.

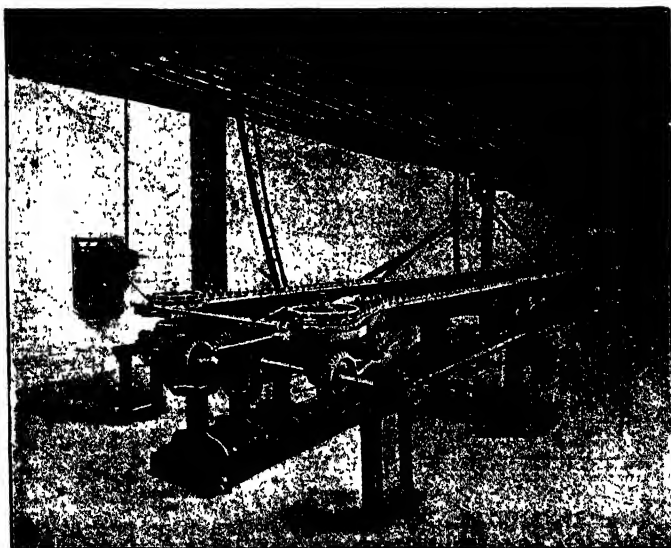


Fig. 168.—Farmer's Stenter.

A stenter consists essentially of two extended horizontal frames, provided with means of supporting and stretching the cloth between them. The distance between the frames is adjustable, and the fabric is gripped close up to the selvages. Thus, in woven goods the tension may be applied directly



at the ends of the weft threads, thereby simultaneously straightening and stretching them while in a damp condition. There are several kinds of stenters, and they may be either stationary or progressive. Fig. 168 shows a common type of the former. The goods are stretched on it, and dried in the stretched condition by means of hot air.

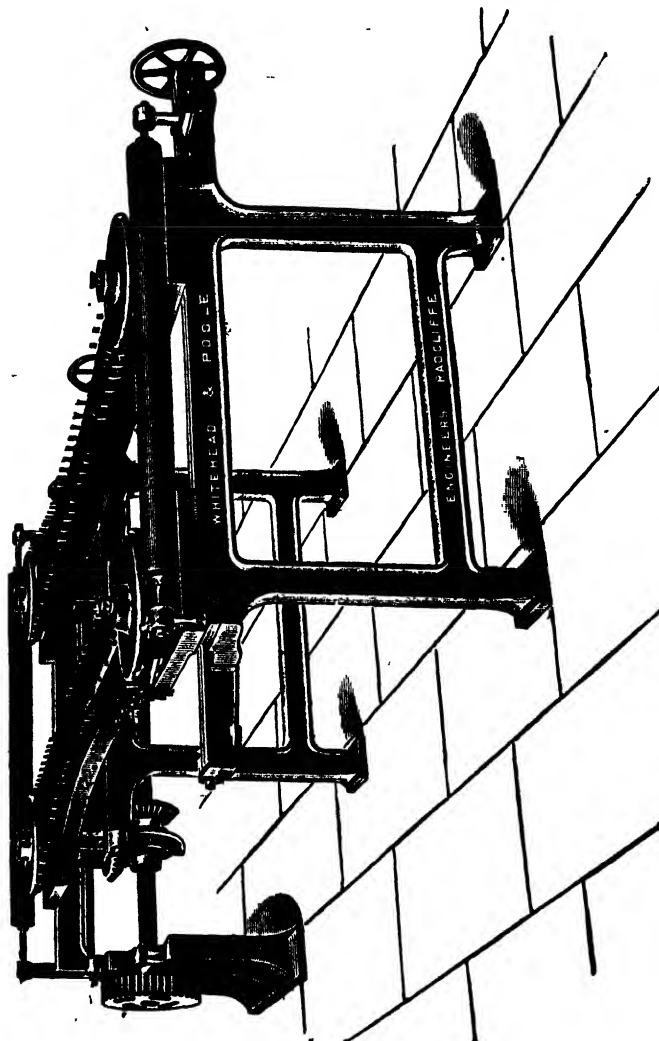


Fig. 169.—Automatic Self-feeding Clip Stretching Machine.

In progressive stenters or *clip stretchers* (Fig. 169), a pair of rails support an endless chain of clips, which seize the cloth, carry it through the machine, and liberate it at the end. The width of the frames can be set to increase from start to finish, thus extending the cloth gradually. The swissing motion is provided for by a worm wheel, which operates swivel brackets upon which the frame is supported. The rate of motion can be adjusted or reduced to zero as desired.

## CHAPTER XXIV.

### DYEING MACHINERY.

**Requirements of Dyeing Machines.**—The essential requirements of a dyeing machine are—

- (1) That it shall provide sufficient movement for the liquor to penetrate uniformly into every part of the goods.
- (2) Although this movement must be sufficient to give penetration, it must not be so severe that it damages fabrics of finer textures or causes milling in the case of wool.
- (3) The machine must be built of a material which will withstand prolonged boiling with acid or alkaline solutions.
- (4) The steam-inlet or other heating agency must be so arranged that a uniform temperature is maintained throughout the liquor.
- (5) There should be some means of adding the concentrated dyestuff solution in such a way that it is well diluted before it comes into contact with the goods.
- (6) Since the wet steamy atmosphere of a dye-house encourages corrosion, it is an advantage to construct a machine with the minimum of parts which cannot be protected against corrosion.

The vast clouds of steam rising from a number of dyeing machines in a confined space can create a very foggy atmosphere. A tendency is now apparent to build totally enclosed dyeing machines, from which no steam can escape during the dyeing operation. Such machines have three distinct advantages: In the first place, there is an appreciable economy of steam, because large surfaces at which cooling can occur are avoided. Secondly, they prevent escape of steam into the atmosphere, thereby improving conditions in the dye-house, and reducing troubles such as corrosion and stains due to condensation of steam on the roof. Thirdly, dyeing is carried out under a slight positive pressure, which raises the temperature two or three degrees. This often results in more level dyeing.

Uniform penetration and level dyeing depend on both mechanical and chemical factors. It is, of course, vitally important that the machine should be constructed so that there is adequate movement of the goods or the liquor. It must never be forgotten, however, that the perfect machine will not give level dyeing unless the proper precautions are taken in the addition of the chemicals and the control of the temperature. In this chapter only the mechanical aspects of level dyeing will be dealt with. Adequate movement is obtained either by moving the goods through the liquor or by forcing the liquor through the material. Generally speaking, movement of the goods is to be preferred, except in those cases where the material is extremely delicate or is of such a nature that movement will cause excessive felting.

**Materials used in the Construction of Dyeing Machines.**—In the past, dyeing machines were universally constructed of wood, and to-day many wooden machines are still used, but, generally speaking, wood has been superseded by better materials.

The wood selected for use must possess sufficient power to endure prolonged boiling. It must also be free from resins, because the latter melt at the boiling-point of water and exude from the wood, causing staining. The cheapest wood suitable for this purpose is Columbian pine. Teak is also commonly used, and machines made from this timber have considerably longer life. Greenheart is the best wood of all, but it is extremely expensive.

All wooden machines possess one serious disadvantage: the acids and dyestuff are absorbed in the pores of the wood, and are liable to come out during the succeeding dyeings, thus upsetting the dyer's formulæ. This makes accurate matching more difficult, and often means that boiling must be continued for a longer period before good matches can be obtained. The longer process time is due to the fact that, since formulæ are affected by the absorbed dye, they are less reliable, and the dyer is therefore compelled to add his colour more cautiously. The longer boiling period is often a distinct disadvantage in wool-dyeing, because it leads to over-milling. Wooden machines are also less versatile from the point of view of production. With these, it is, *e.g.*, not possible to dye light shades after heavy ones; thus certain machines have to be reserved for bottle greens, nigger brown, scarlet, navy blues, etc. Orders do not always come in so adjusted that they correspond exactly with the capacities of the machines which have been reserved, and it is therefore extremely inconvenient if it is not possible to change from one shade to another on a machine. Finally, it is practically impossible to dye very clear shades in wooden machines, owing to the difficulty experienced in bringing the vessel to an adequate state of cleanliness.

For these reasons, numerous attempts were made over many years to find a more satisfactory material. Synthetic resins, enamel linings, and ebonite linings were tried, but with comparatively little success. The problem was, however, solved when stainless steel became available. In itself, stainless steel is the perfect material for making dyeing machines, although in the early days considerable difficulty was experienced in making satisfactory joints. Solder and spot welding were used, but both methods had disadvantages. Welding was not at that time practicable because the resisting power of the stainless steel was destroyed by heat. At a later date, stainless steel which could be welded became available, and this resulted in a great advance in dyeing-machinery construction.

All modern dyeing machines are constructed of stainless steel, and this has led to great improvements in dyeing technique. Formulæ can be relied upon to a far greater extent. A greater production is possible from the same number of dyeing machines, owing to the fact that no machine is restricted to the dyeing of one particular depth of shade. There has also been a marked improvement in the brightness and clarity of colours obtainable, and this applies particularly to the paler shades.

**Machines for Dyeing Yarn.**—In yarn-dyeing, two different principles of obtaining sufficient agitation are made use of. Either movement of the yarn through the liquor or movement of the liquor through the yarn is relied upon. Generally speaking, better penetration is obtained by movement of the yarn through the liquor, but in the case of wool yarns, which felt, or of very fine yarns, which are liable to become entangled, movement of the liquor is to be preferred.

*Bobbin Type of Machine.*—This machine (Fig. 170) is used extensively for dyeing cotton or rayon yarns. It consists essentially of a number of porcelain

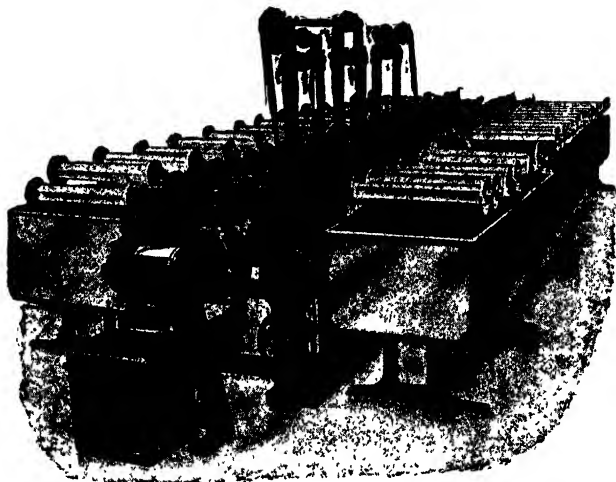


Fig. 170.—Bobbin-type Yarn-dyeing Machine.

bobbins, which are mechanically rotated, and to which a vertical movement is also imparted. The hanks are rotated through the liquor, at the same time

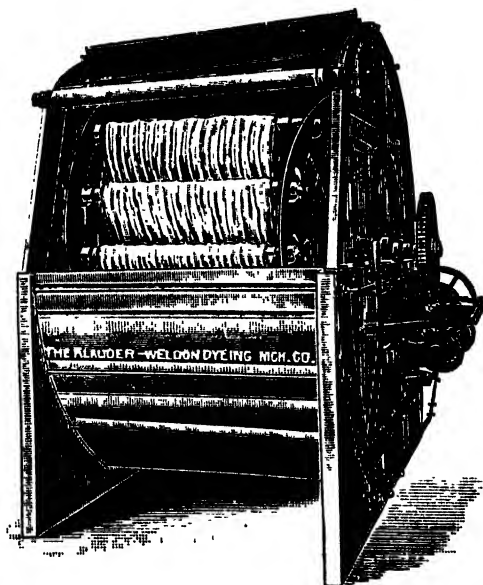


Fig. 171.—The Klauder-Weldon Dyeing Machine.

being moved upwards and downwards, which has the effect of opening the hanks and allowing the liquor to penetrate into the centre of the yarn.

*Klauder-Weldon Dyeing Machine.*—In this machine (Fig. 171) the yarn is

held by poles carried near the centre and at the circumference of two large discs. The discs carrying the poles rotate on an axle, thereby alternately dipping the yarn into the dye liquor and then lifting it out again. This machine was commonly used at one time, but is not made use of to the same extent to-day.

*Cheese-dyeing Machines.*—Cheese-dyeing machines have, in the past, been used mainly for dyeing cotton, but there is now an increasing tendency for them to be used for wool. An example of a cheese-dyeing machine is shown in Fig. 172. The yarn is wound on to perforated stainless-steel spools, which are slipped over a perforated tube attached to a force pump. The dye solution is forced through the spools by the pump, thus ensuring that the liquor

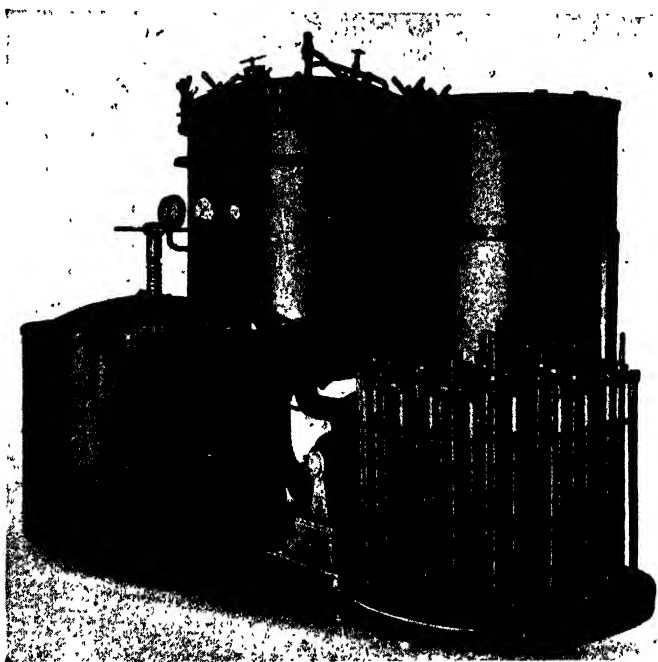


Fig. 172.—Cheese-dyeing Machine.

will reach every part of the charge in the machine. This type of dyeing machine is particularly suitable for yarns of very fine count. There is absolutely no disturbance of the threads, which eliminates difficulty in winding. The dyed yarn is very easily wound off the spools on to cones or whatever form of package is needed.

*Hussong Dyeing Machine.*—This is by far the most commonly used machine for dyeing wool yarns. An example is illustrated in Fig. 173. It consists essentially of a frame, carrying poles on which the yarn is hung, which can be lowered into a rectangular vessel containing the dye liquor. The liquor is circulated by means of a propeller, which is situated behind a grid intended to prevent the yarn from coming into contact with the propeller. The construction of the machine is explained by the sectional diagram shown in Fig. 174. The packing of the yarn on the poles is an important factor if the best results are to be obtained from this machine. The flow of the liquor will

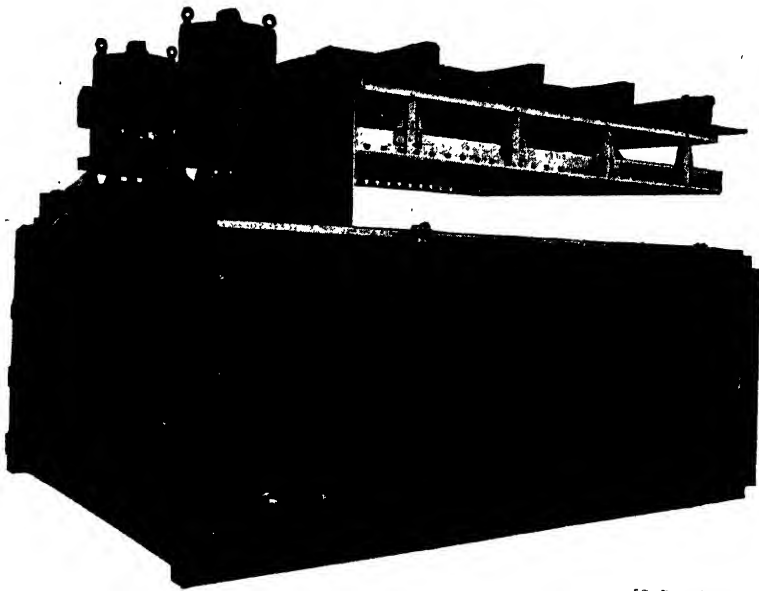


Fig. 173.—Hussong Dyeing Machine.

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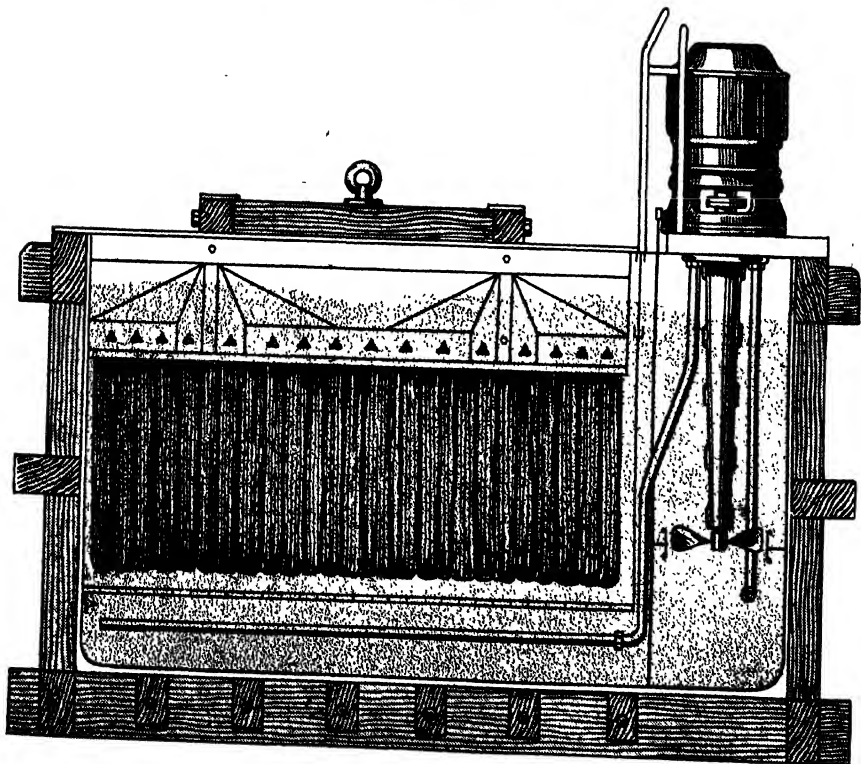


Fig. 174.—Sectional View of Hussong Dyeing Machine.

[S. Pegg & Son.

tend to take the course which offers the least resistance. If the yarn is not distributed evenly, but is packed tighter in some places than in others, the bulk of the liquor will flow through those parts where the packing is loose, and uneven dyeing will result.

The machine is provided with a two-way switch, so that the direction of the current can be reversed when desired. During dyeing the direction of

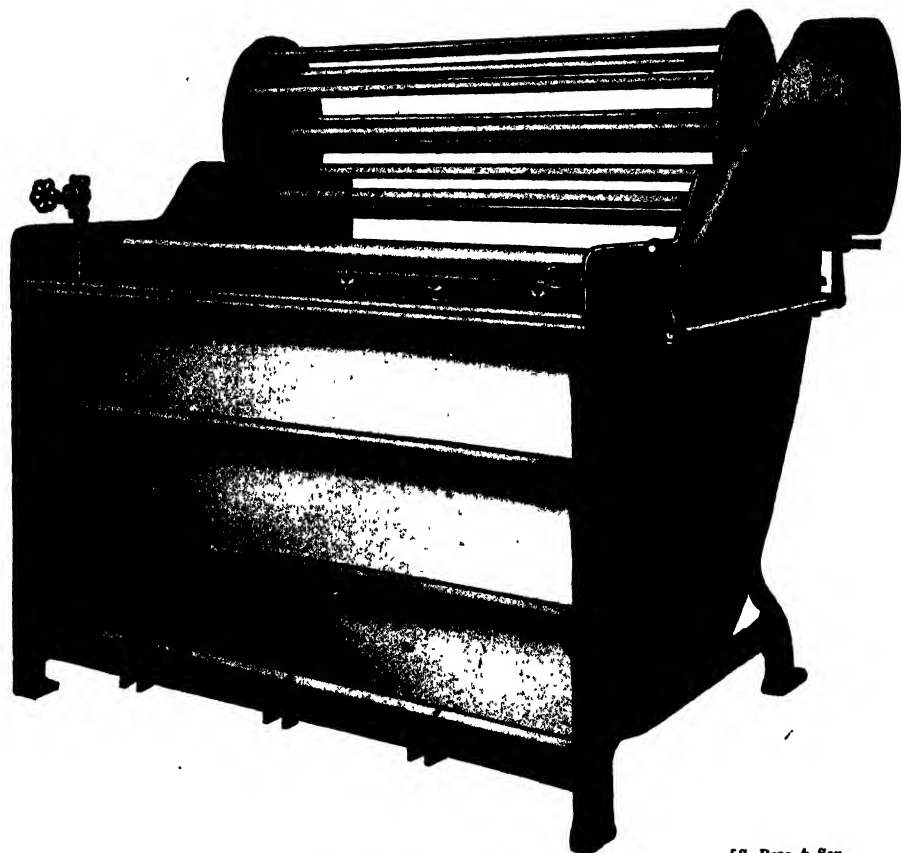


Fig. 175.—Fabric-dyeing Machine.

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the flow should be reversed from time to time. When the flow is downwards, the liquor does not come into sufficiently intimate contact with the portion of the hank resting on the pole. This would result in light patches on every hank if the flow were not reversed to the upward direction, which lifts the hank off the pole.

Small Hussong machines for dyeing 5-lb. and 10-lb. sample lots are obtainable, as well as machines for handling batches as large as 1000 or 1500 lb.

**Fabric-dyeing Machines.**—Practically without exception, fabrics and cloths are dyed in various types of winch machines; a typical one is shown in Fig. 175. The machines are constructed in various sizes, the following capacities being most commonly found in dye-houses: 50, 150, 250, and 400 lb.

The pieces are loaded on to the machine by throwing one end over the winch, holding the other end in the barrow. The end thrown over is threaded under the guide rods and joined to the end in the barrow, an endless chain being made out of the material. The web is run into the machine, and the rotation of the winch causes the endless chain to move through the liquor continuously throughout the whole of the dyeing operation.

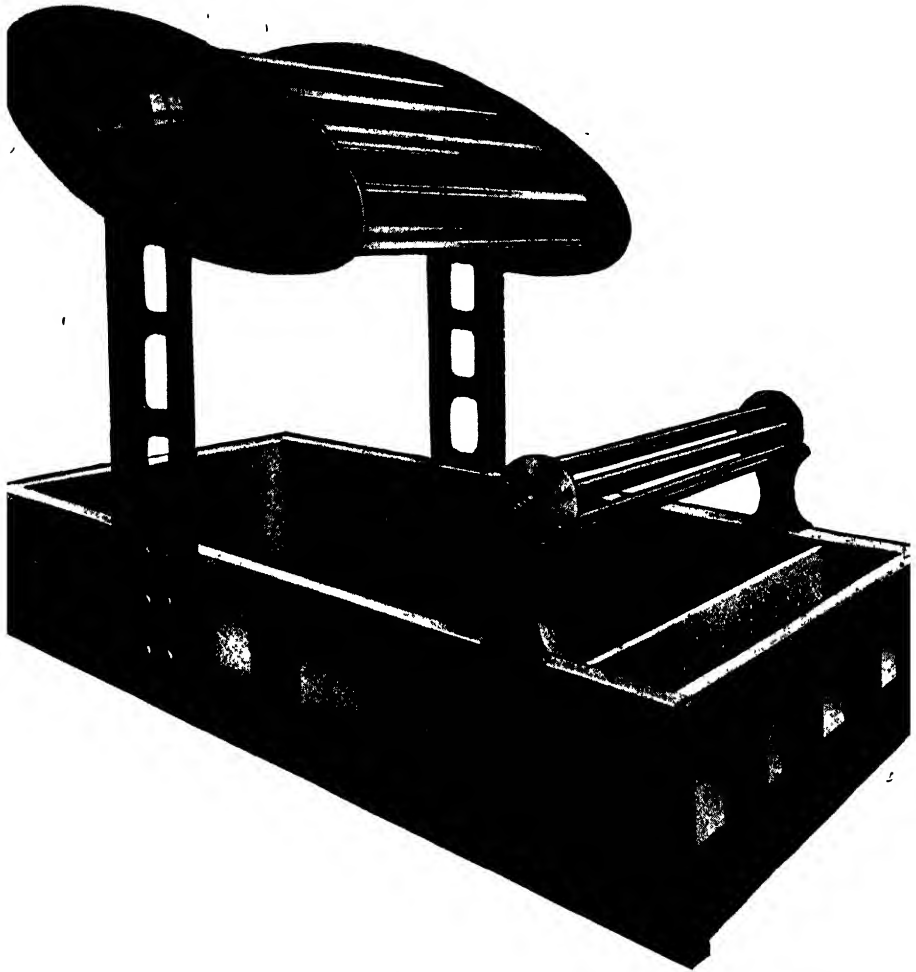


Fig. 176.—Machine for Dyeing Acetyl Fabrics.

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The speed of the machine should be adjusted according to the nature of the material to be dyed. Obviously, the greater the amount of movement the more uniform will be the dyeing. With wool fabrics, however, excessive movement causes undesirable felting or shrinkage. With wool, therefore, a slow-running machine is to be recommended, bearing in mind always that excessive slowing will lead to unlevel dyeing. With cotton and rayon fabrics there is no danger of felting, and a fast-running machine is to be preferred,



except in those cases where very delicate materials, which are easily damaged, have to be dyed.

As the cloth or web falls into the liquor from the winch at the back of the machine, it tends to bunch up and to lie in a heap for a short interval. This is no disadvantage with wool and cotton fabrics, but tends to cause serious creasing with acetyl rayons. To overcome this, a long shallow machine with an elliptical winch (Fig. 176) is used for acetyl fabrics. The elliptical winch folds the material into deep layers as it falls, and these are free from random creases (other than those at the folds). The shallowness of the machine means

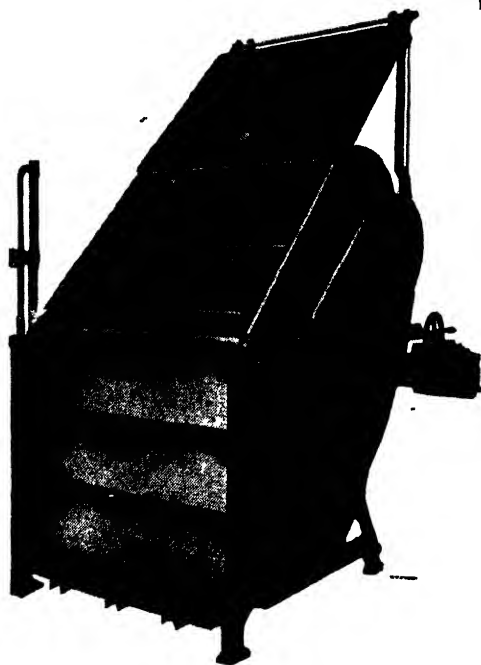


Fig. 177.—Enclosed Fabric-dyeing Machine.

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that there is no great weight of liquor pressing on the fabric to make the creases permanent.

The latest development in cloth- or fabric-dyeing is the totally enclosed machine: in the past the liquors have always been exposed to the air. Enclosed machines such as the example shown in Fig. 177 have advantages which have already been referred to earlier in this chapter.

**Footwear- and Garment-dyeing Machines.**—The machine most commonly used for dyeing wool stockings and socks is the paddle type illustrated in Fig. 178. The paddle gives very efficient movement of the goods, which is particularly necessary in the case of stockings or socks which have seams which are difficult to penetrate, or where there is a tendency for the heels to resist penetration. The circulation is generally assisted by deflecting upwards the flow of steam supplied through pipes at the bottom for heating the liquor. Goods are then not allowed to settle in the bottom and thereby to escape the movement imparted by the blades of the paddle. There is an

island in the middle with perforated sides, through which addition of the dyestuff may be made.

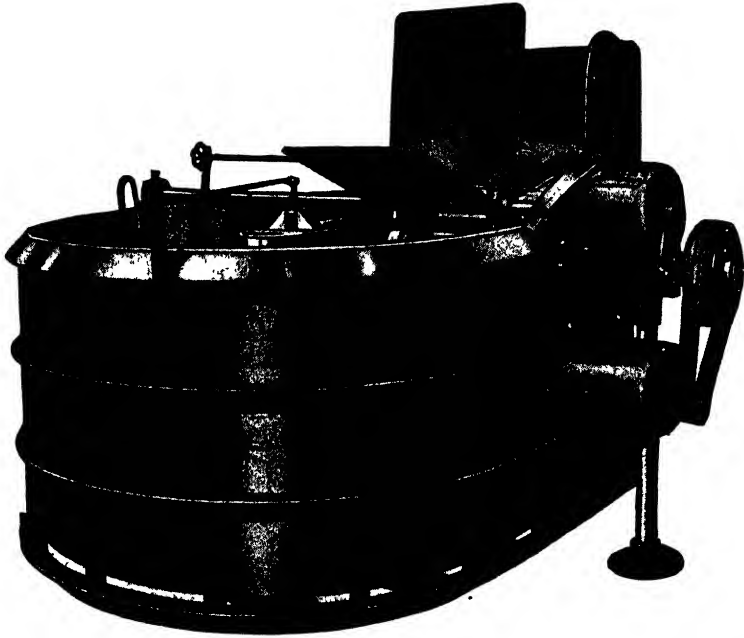


Fig. 178.—Footwear-dyeing Machine.

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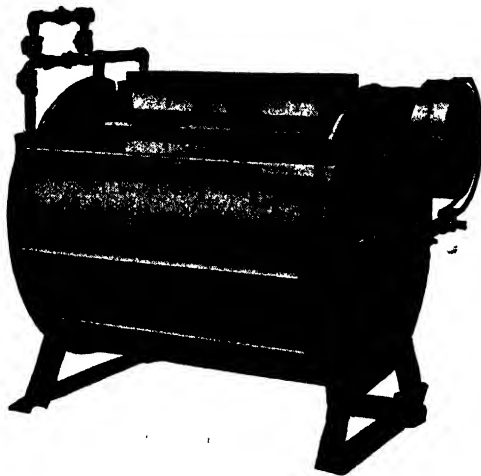


Fig. 179.—Stocking-dyeing Machine.

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The movement of the machine is sometimes too drastic for finer wool garments or for rayon stockings. The machine with the longer and shallower paddle shown in Fig. 179 is gentler in its action, and is therefore sometimes preferred.

The uniflow type of machine, which is used for dyeing garments, is often favoured on account of its simplicity of construction (Fig. 180). This machine contains no moving parts, and requires no mechanical drive. It can therefore be erected wherever steam is available. It will be noticed that the machine has one side which is semi-cylindrical in shape. The steam used for heating leaves the supply pipe in such a way that it drives the water towards this curved surface, where it is deflected so that a strong circular flow is imparted to the liquor. This movement of the water carries the goods with it, and

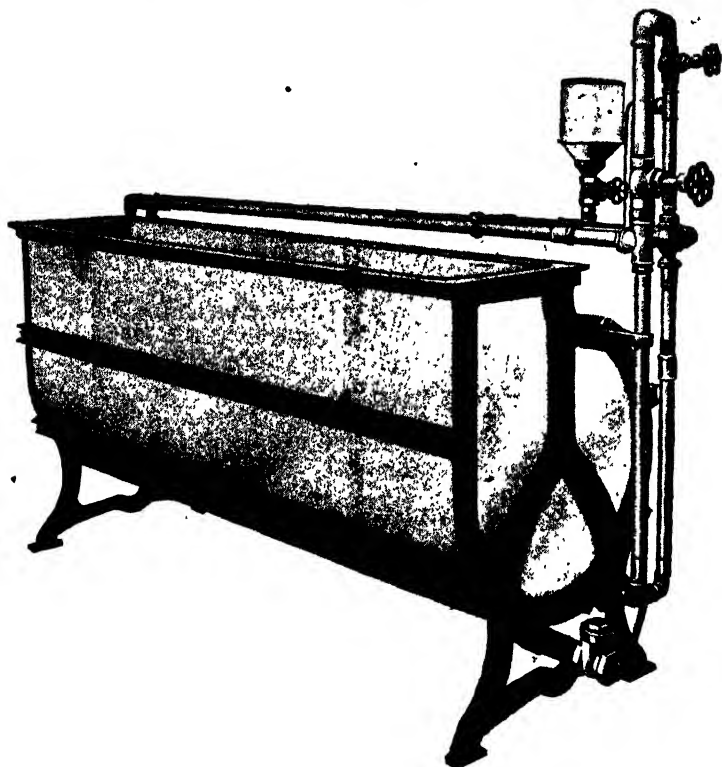


Fig. 180.—Uniflow Garment-dyeing Machine.

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maintains the agitation necessary for penetration and level dyeing. These machines are generally used for smaller batches, but are not so successful for larger weights, such as 200 and 300 lb.

Silk hosiery is always dyed in the Smith Drum type machine. This is shown in Figs. 181 and 182. The machine consists of an inner perforated drum with sliding doors, which carries the stockings (Fig. 182). Silk goods, when degummed and in the wet state, are very easily damaged by the minutest rough surfaces or even scratches in this drum. A very high finish is therefore given to it to ensure perfect smoothness. The machine consists of an outer case (Fig. 181), which contains the liquor in which the inner drum rotates. A reciprocating movement is given to the drum, so that it rotates for several revolutions in one direction and then for an equal number in the opposite direction.

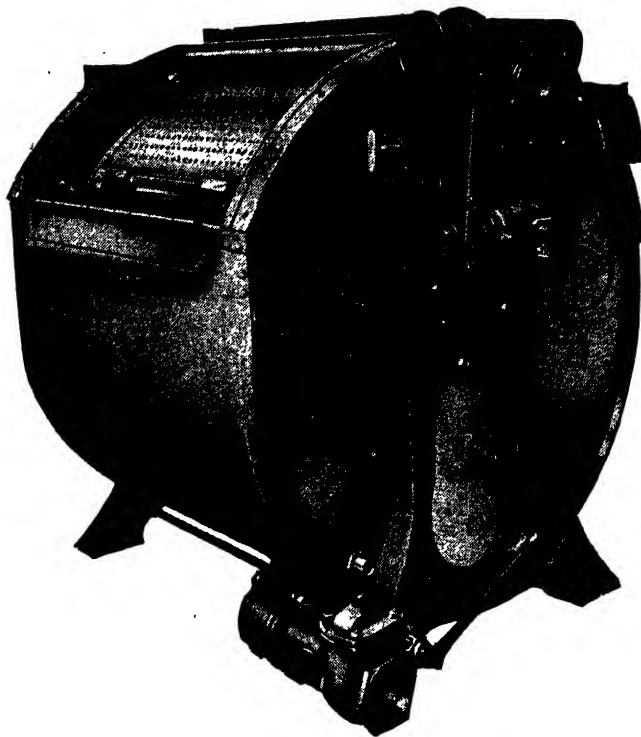


Fig. 181.—Motor-driven 100-lb. Smith Drum Machine.

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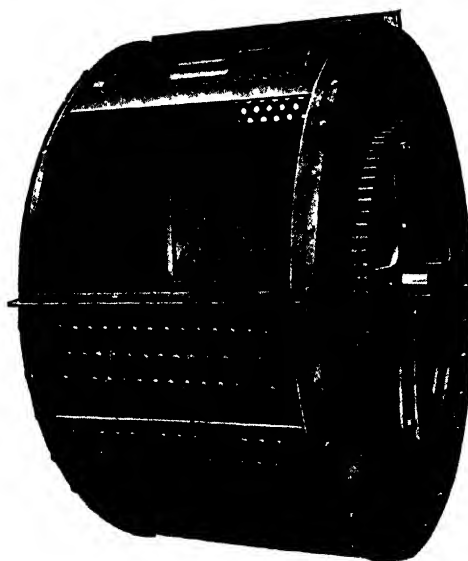


Fig. 182.—Cylinder from a 50-lb. Smith Drum Machine.

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*Dyeing Jigger.*—The dyeing jigger (Fig. 183) is the machine most commonly used for cotton or rayon and woven piece-goods, which are dyed with direct cotton colours, where exhaustion is not good. In order to achieve the greatest economy in the use of dyestuffs, short liquor is essential. The winch machines which have been described for dyeing fabrics cannot be operated without using a fairly high liquor ratio, because practically the whole of the material

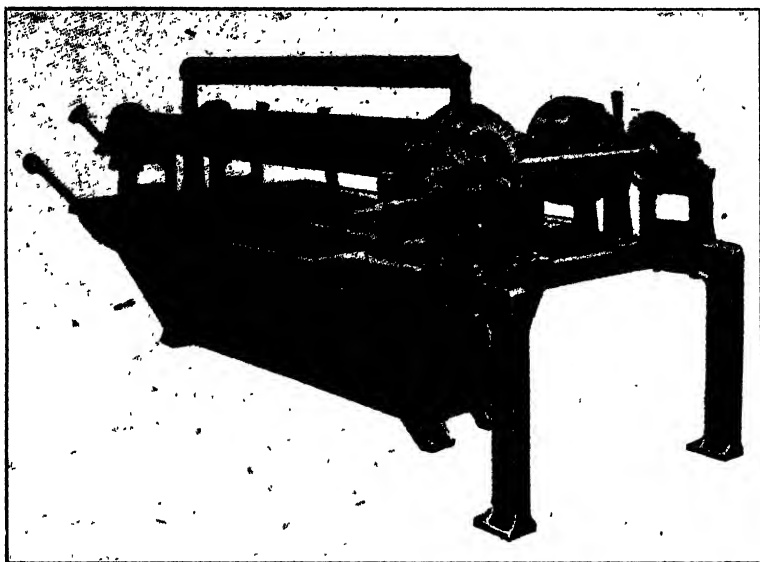


Fig. 183.—Dyeing Jigger.

must be immersed. In the jig, however, the material is wound over rollers standing above the liquor, and these rotate alternately in a clockwise and an anticlockwise direction. The fabric passes through a relatively shallow trough, containing the dye solution, which is fitted with two more guide rollers at the bottom to ensure complete immersion of the material. Only a few yards of the piece are immersed in the dye-bath at any one time, and this makes it possible to work with a short liquor. The necessary movement to ensure uniform penetration is obtained by pulling the length of the material off one roller, through the liquor, and on to the other, and repeating the operation in the reverse direction.

## CHAPTER XXV.

### THE ACID DYESTUFFS.

THE acid dyestuffs owe their name, firstly, to the fact that they are generally used in a bath containing free sulphuric or other acid, and, secondly, to the fact that they are nearly all sodium salts of organic acids, the acid being the active dyeing principle, which apparently enters into combination with the fibre. The acid is in nearly every case a sulphonic acid, though in a few dyestuffs it is an ordinary carboxylic acid, i.e. it contains one or more  $\text{-COOH-}$  groups. The sodium salts of these acids are readily soluble in water, whereas the free acids are often only sparingly soluble, and are sometimes hygroscopic. Further, it is easier to prepare the sodium salt than the free acid.

The acid dyestuffs are of great importance, since they dye animal fibres directly, without the intervention of a mordant. They have, however, no affinity for cotton and other vegetable fibres. They are used very extensively for both wool and silk.

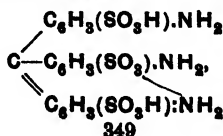
The group includes a very large number of dyestuffs, with an extensive range of colours. The acid dyestuffs have not so great a tinctorial power as the members of some other classes, about 5 per cent. being required to give a full shade on wool. The colours vary in fastness. Some are much faster than others, but, as a rule, they are not particularly fast to washing with soap and water, and are in nearly all cases stripped from dyed fabrics by a boiling dilute solution of ammonia or sodium carbonate. They give faster colours on silk than on wool.

**Types of Acid Dyestuffs.**—(1) *Nitro Compounds.*—Picric acid,  $\text{C}_6\text{H}_2(\text{NO}_2)_3.\text{OH}$ , is the oldest member of this class, but is no longer used. 2:4-Dinitro- $\alpha$ -naphthol, or Naphthol Yellow,  $\text{C}_{10}\text{H}_6(\text{NO}_2)_2.\text{OH}$ , is a useful dyestuff, but has only a limited solubility. When, however, it is sulphonated, the product, 2:4-dinitro-1-naphthol-7-sulphonic acid (sodium salt), is readily soluble in water, and gives a good yellow on wool.

(2) *Nitroso Compounds.*—These contain the nitroso group,  $\text{-NO}$ , as chromophore. Naphthol Green B is an example.

(3) *Sulphonated Azo Compounds.*—These contain the  $\text{-N=N-}$  group as the chromophore, and are made by coupling a diazo compound with a sulphonic acid which contains an auxochrome group. The diazo compound may also be coupled with an amino or hydroxy compound, and sulphonated afterwards. Orange II,  $\text{NaO}_3\text{S.C}_6\text{H}_4.\text{N:N.C}_{10}\text{H}_6.\text{OH}$ , is an example; another is Ponceau 4GB, which has been described above (p. 7).

(4) *Sulphonated Basic and Other Dyestuffs.*—Many dyestuffs belonging to other classes are changed to acid dyestuffs by sulphonation. The leuco base of pararosaniline,  $\text{HO.C:}(\text{C}_6\text{H}_4.\text{NH}_2)_3$ , when sulphonated becomes

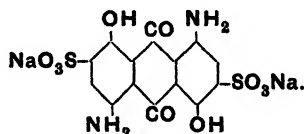


which is present in Acid Magenta. Aminoazobenzene hydrochloride,  $C_6H_5.N:N.C_6H_4.NH_2.HCl$ , is a basic dyestuff, converted into Acid Yellow,  $NaO_3S.C_6H_4.N:N.C_6H_4(SO_3Na).NH_2$ , when treated with fuming sulphuric acid. Another example is Indigo Carmine, which is sodium indigo-disulphonate,  $C_{16}H_8N_2O_2(SO_3Na)_2$ .

(5) *Eosines*.—These are all sodium salts of carboxylic acids. Rhodamines are very similar, but are used generally as basic dyestuffs.

(6) *Ionamines* are  $\omega$ -sulphonic acids, i.e. sulphonic acids in which the  $SO_3H$  group is not attached to a carbon atom of the aromatic residue. The  $\omega$ -methylene sulphonic acid of aminoazobenzene,  $C_6H_5.N_2.C_6H_4.NH.CH_2.SO_3Na$ , is an ionamine used in dyeing acetyl silk and wool.

(7) *Solway Dyestuffs*.—These dyestuffs, such as Solway Blue B, are derivatives of anthraquinone, and dye wool from an acid bath. Solway Blue has the formula:



(8) *Acid Mordant Dyes*.—A mordant is a substance which can form an insoluble compound with a dyestuff. Acid mordant dyes contain hydroxyl as well as either carboxyl or sulphonic-acid groups. Since the hydroxyl group is characteristic of mordant dyes, these dyestuffs have at the same time the properties of both classes. By reason of their acid nature they dye wool and silk directly from an acid bath. But since they are also mordant dyes, they can be more firmly fixed on the fibre by means of a mordant such as chromium oxide,  $Cr_2O_3$ . When the true mordant dyes are used, the wool must be mordanted first, and then dyed: thus two distinct operations are necessary. With the acid mordant dyes the wool can be dyed first, and then mordanted on the fibre in the same bath by adding a solution of the mordant (potassium dichromate). This operation is termed *after-chroming*, and the dyes are sometimes called *after-chromed colours*. The mordanting generally alters the shade, but produces colours which are much faster than those given by the ordinary acid dyes, and on this account is largely used in wool-dyeing.

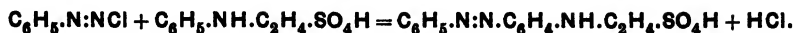
Another similar group contains the *chromotrope dyestuffs*, which can be used either as acid or as acid mordant dyes. These are all derivatives of *chromotropic acid*, which is 1:8-dihydroxynaphthalene-3:6-disulphonic acid, having the formula  $C_{10}H_4(OH)_2(SO_3H)_2$ . When this acid is coupled with diazotized amines, chromotrope dyes are obtained. For example, Chromotrope 6B is made by coupling the diazonium salt of para-aminoacetanilide,  $CH_3.CO.NH.C_6H_4.NH_2$ , with chromotropic acid, thus:



The *metachrome* or *monochrome dyestuffs* are treated sometimes as acid dyestuffs. They will be dealt with later.

(9) *Sulphato Dyestuffs*.—These dyestuffs were discovered by Green and Saunders (*J. Soc. Dyers Col.*, 1923, 39, 39). Instead of sulphonic-acid groups they contain one or more  $NH.C_6H_4.SO_3H$  or  $N:(C_6H_4.SO_3H)_2$  groups, the dyestuffs having the general formula  $R.NH.C_6H_4.SO_3H$  or  $R.N:(C_6H_4.SO_3H)_2$ . The group  $-SO_3H$  is termed the *sulphato group*. A simple example is a soluble

yellow dyestuff obtained by coupling diazobenzene chloride with sulphato-ethylaniline, thus:



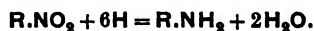
The dyestuff is the sodium salt of this sulphato acid. Sulphato Scarlet is made by coupling diazotized *p*-nitro-aniline with the sodium salt of ethyl sulphato-ethylaniline.

(10) *Fast Acid Dyestuffs*.—Certain of the acid dyestuffs are notably fast to the action of alkalis and to milling. They contain, in addition to sulphonic-acid groups, others which either give them basic properties or make them similar to the direct or mordant dyes in structure. Acid Violet, for example, contains amino and substituted-amino groups, which have a direct affinity for wool. Milling Scarlet, another example, contains both sulphonic and hydroxyl groups.

(11) *Neolan Dyestuffs*.—These contain hydroxyl-sulphonic acid and a metal such as copper; for example, diazotized 1:2:4 amino-naphthol-sulphonic acid (Na salt) is coupled with the sodium salt of 1:5 naphthol-sulphonic acid in presence of a copper salt. They are used in a strongly acid bath.

**General Properties of Acid Dyestuffs**.—Acid dyestuffs are soluble in water, and their aqueous solutions are generally colloidal. They are in many cases soluble in alcohol or amyl alcohol. All are precipitated from their aqueous solutions by saturating them with salt or sodium sulphate, and commercial samples commonly contain these salts as impurities. They combine with basic dyestuffs, and cannot be used with them except under special conditions. They give insoluble precipitates in some cases with basic oxides. If an acid is added to an aqueous solution of an acid dyestuff, the sulphonic acid is liberated. The acids are often sparingly soluble in water, and hence form precipitates. When the dyestuff is the sodium salt of a carboxylic acid, the dye acid can be extracted from the acidified solution with ether. The sulphonic acids are generally sparingly soluble in amyl alcohol or butyl alcohol. In some cases the dye acids can be prepared by precipitating the lead salt and decomposing this with sulphuretted hydrogen.

When acid dyestuffs are treated with a reducing agent, they are generally decolorized, giving in some cases *leuco* compounds. These are formed when hydrogen is absorbed without decomposition of the compound. Thus indigo carmine,  $\text{C}_{16}\text{H}_8\text{N}_2\text{O}_2(\text{SO}_3\text{Na})_2$ , takes up two atoms of hydrogen, giving  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2(\text{SO}_3\text{Na})_2$ , which is a colourless compound. When it is oxidized, these hydrogen atoms are removed as water, and the colour reappears. When an azo dyestuff is reduced, it gives a mixture of amines, and the dyestuff cannot be reproduced by oxidation. Thus, Croceine Orange,  $\text{C}_6\text{H}_5\text{.N:N.C}_{10}\text{H}_7(\text{OH}).\text{SO}_3\text{Na}$ , gives, when reduced, aniline,  $\text{C}_6\text{H}_5\text{.NH}_2$ , and the compound  $\text{NH}_2\text{.C}_{10}\text{H}_7(\text{OH}).\text{SO}_3\text{Na}$ . Nitro compounds when reduced give amines, and hence are decomposed permanently; thus:



For purposes of dyeing, acid dyestuffs may be divided into three classes, viz. (i) those which require the assistance of a strong acid; (ii) those with which a weak acid is sufficient; and (iii) those which can be used without an acid. In all cases the dye acid must be liberated in the bath. In the third class this is accomplished by hydrolysis, in the other two by the weak or strong acid respectively.



### Assistants.

In practice, goods are rarely dyed in a solution of the dyestuff in water alone. Certain chemicals, termed *assistants*, are always added to the bath. These act in various ways: they may (i) increase or decrease the solubility of the dyestuff in the bath; (ii) liberate the essential constituent of the dyestuff; (iii) accelerate or retard the deposition of the dyestuff on the fibre; (iv) assist penetration; and (v) affect the degree of dispersion of the dyestuff. In the case of acid dyestuffs the assistants used are an acid and Glauber salt. The acid may be either sulphuric acid, formic acid, or acetic acid. The way in which these assistants act has been the subject of much work and discussion, which may be dealt with briefly.

**Function of the Acid.**—Comparatively few of the acid dyes will dye wool unless an acid is present in the bath. If, for example, wool is boiled gently for half an hour with about twenty times its weight of water and 5 per cent. of acid magenta, it is only faintly stained. If from 4 to 5 per cent. of sulphuric acid is also added, the wool will be dyed. The first action of the acid is to decompose the dyestuff, liberating the sulphonc acid, but a considerable excess is essential for dyeing. Both mineral acid and dye acid are taken up by the wool, and the quantity of the former determines the quantity of the latter up to a certain point. This is illustrated by the results given in Table LIV (Trotman and Horner, *J. Soc. Dyers Col.*, 1934, 50, 66), obtained with indigo carmine. The authors concluded as the result of many experiments that: (i) the maximum quantity of dye absorbed depends upon the amount of sulphuric acid present in the dye-bath; (ii) the acid is absorbed rapidly during the first 15 min. after introducing the wool, but very little is taken up afterwards; (iii) when a high percentage of dye is present, its rate of absorption is more rapid than that of the acid during the first 30 min. of dyeing, but does not reach a maximum so quickly as that of the acid; (iv) when the percentages of acid and dye are comparable with those used in commercial dyeing, the rate of absorption of the acid is more rapid than that of the dye, and reaches the maximum more quickly; and (v) the relative rates of absorption of acid and dye are determined by the percentages of each present and the concentration of the bath with respect to the acid.

TABLE LIV.—EFFECT OF ACID ON ABSORPTION OF INDIGO CARMINE.

(Weight of wool, 5 g.; volume of liquor, 150 ml.; percentage of dye, 10.)

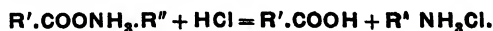
Sulphuric Acid used, per cent.	Dye absorbed, per cent.	Acid absorbed, per cent.
0.0	0.90	..
1.0	2.49	..
2.0	5.64	..
3.0	7.53	..
4.0	8.47	..
6.0	8.53	3.45
8.0	8.75	3.88
10.0	8.81	4.32
12.0	8.89	4.74
15.0	8.95	4.90
20.0	9.00	5.30

It is obvious that the liberation of the dye acid is only one function of the mineral or other acid, and the free dye acid has little affinity for wool in the absence of acid. The action of the acid was thought at one time to be that of increasing the basic groups of the wool by hydrolysis of the protein. Suida (*J. Soc. Chem. Ind.*, 1909, **28**, 112) and Fort (*ibid.*, 1913, **32**, 907) held this opinion. Justin Mueller (*ibid.*, 1909, **28**, 906) considered that the action of acid was to decrease the solubility of the dye acid. This, however, could hardly be the case, since the dye acids are all only slightly soluble in water. Haldane, Gee, and Harrison (*ibid.*, 1910, **29**, 484) applied the electric theory of dyeing to explain the function of the acid. Both wool and silk become negatively charged in contact with water. The acid dyestuff ionizes into  $R.SO_3^-$  and  $Na^+$  ions. The  $R.SO_3^-$  ions are negatively, and the  $Na^+$  ions positively, charged. Now if the wool is also negatively charged, it cannot combine with the similarly charged dye-acid ions. But as soon as the charge on the wool becomes positive, which it does at  $140^\circ F.$  ( $60^\circ C.$ ) in the presence of an acid, it attracts and combines with the oppositely charged dye-acid ions.

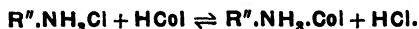
All of these theories of the dyeing of wool with acid dyes, except the last, depend ultimately on the affinity of the amino groups for the dye acid, *i.e.* are purely chemical theories. But with regard to these it must be remembered that, whilst wool absorbs acids from their aqueous solutions, the compounds formed are not very stable, and moreover the  $CO.NH$ -groups have to be taken into account. E. R. Trotman (*J. Soc. Dyers Col.*, 1924, **40**, 74) found that de-aminated wool had the same affinity for acid dyestuffs as unde-aminated wool, and Paddon (*J. Physical Chem.*, 1922, **26**, 384) obtained the same results. This indicates that amino groups are not concerned in dyeing. Speakman (*J. Soc. Dyers Col.*, 1922, **38**, 384) said that de-amination merely brought the  $CO.NH$ -groups into action, and since these outnumber the amino groups, one would not expect de-amination to have much effect on the affinity for dyestuffs. In a later paper Speakman and Stott described a new method for de-aminating wool, and found that the product had a decreased affinity for acid dyestuffs.

Recent work on the theory of acid dyeing has been concerned chiefly with the effect of hydrogen-ion concentration, and the physical and chemical changes induced in the wool by water and acid. Elöd regarded  $pH$  as the chief factor in dyeing, the maximum quantity of dye acid being taken up at  $pH$  1.3.

Speakman (*J. Soc. Dyers Col.*, 1933, **49**, 189) gave the following explanation of the action of acid: Hot water increases the size of the intermicellar spaces of wool, and opens up the structure of the micelles. Since the latter consist of long peptide chains bridged across by salt linkages, the process of micelle subdivision is accelerated by acids. In acid solutions the salt linkages are separated by reactions of the type:



In presence of colour acid ( $HCol$ ) double decomposition then takes place:



The amount of combined colour acid is determined by a number of factors, *e.g.* (i)  $pH$ , (ii) size of dye particle, (iii) size of intermicellar spaces, and (iv) electric charges. It should be noted that this theory, like that of Fort, which will be referred to later, requires that mineral acid is first taken up and then displaced by dye acid.

There is another point to be considered. Acid dyestuffs tend to form

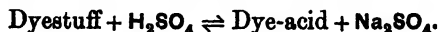
colloidal solutions. For dyeing to take place, the dyestuff micelles must be sufficiently small to penetrate the intermicellar spaces of the wool. It is probable that this subdivision of the dye particles is assisted by the acid in the bath. Goodall (*J. Soc. Dyers Col.*, 1938, **54**, 45) has shown that the sorption of dyes by wool is much affected by the particle size of the dye in relation to the swelling of the fibre under any particular conditions. A molecularly dispersed dye like Acid Orange GG can give the same shade at nearly all temperatures, whilst a colloidal dye cannot.

**Glauber's Salt**,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , is used as a levelling agent, but sodium chloride may be substituted. For a full shade, from 20 to 25 per cent. on the weight of the goods is required, less being necessary for light shades. As a general rule, with quantities of dye up to 2 per cent., 10 per cent. of Glauber's salt is used, and above 2 per cent. of dyestuff 15 to 25 per cent. If wool is dyed with the dyestuff and acid alone, the deposition of the dye is very rapid. A very important rule is that *good dyeing is slow dyeing*. Quick dyeing is liable to give patchy results, since the liquor does not penetrate the fibre completely. This causes the dye to be deposited chiefly on the surface, and makes it liable to rub off. The sodium sulphate retards the rate of adsorption, and thus enables the dye to penetrate into the interior of the fibre. This action, like that of sulphuric acid, is not easy to explain. It has been suggested that the Glauber's salt increases the solubility of the dye in the bath, thus diminishing its solubility in the fibre. Large quantities of sodium sulphate will actually strip the dye from dyed wool. Another view is that it forms sodium bisulphate with the sulphuric acid:



and that sodium bisulphate is less energetic in its action than sulphuric acid. But in this case there would be no advantage in adding more Glauber's salt than is required to convert all the sulphuric acid into bisulphate, while in practice a large excess is necessary. Again, it may act by retarding the rate of dissociation of the dye into its ions. It is a general rule that dissociation is affected by the presence of neutral salts of the same acid.

Another theory is that of Fort (*J. Soc. Chem. Ind.*, 1913, **32**, 907; 1914, **33**, 359). He starts with the view that a dye acid combines with the  $\text{NH}_2$ -groups of the wool to form salts analogous to rosaniline hydrochloride. In the dye-bath the dye acid is liberated in accordance with the reversible equation:

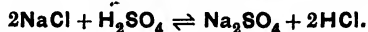


On the fibre a hydrated form of wool is first formed. This combines with sulphuric acid, forming a sulphate. The wool sulphate then reacts with the sodium salt of the dye acid (i.e. dyestuff), producing sodium sulphate and a compound of wool with dye acid. These reactions are illustrated by the following equations, where the dyestuff is represented by the formula  $\text{R} \cdot \text{SO}_3\text{Na}$ :

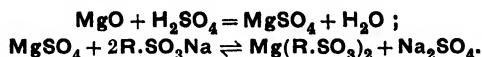
- (1) Wool + Water  $\rightleftharpoons$  Wool hydrate.
- (2) Wool hydrate +  $\text{H}_2\text{SO}_4 \rightleftharpoons (\text{Wool}) \text{H}_2\text{SO}_4$ .
- (3)  $(\text{Wool}) \text{H}_2\text{SO}_4 + 2\text{R} \cdot \text{SO}_3\text{Na} \rightleftharpoons (\text{Wool}) (\text{R} \cdot \text{SO}_3\text{H})_2 + \text{Na}_2\text{SO}_4$ .

These equations show why an excess of sulphuric acid, over that required to set free the dye acid, is needed, for the sulphuric acid is required to form the compound,  $(\text{Wool}) \text{H}_2\text{SO}_4$ . Further, the equation is reversible, and it has already been explained that an excess of any compound taking part in a reversible reaction will tend to drive it towards that side of the equation in

which the compound is not found. Therefore an excess of Glauber's salt ( $\text{Na}_2\text{SO}_4$ ) will drive the equation from right to left, and so tend to keep the dyestuff off the fibre. Glauber's salt is not the only salt which tends to keep acid dyes off the fabric, for the presence of sodium chloride in the bath has a similar but less marked effect. The action of sodium chloride may be due to the formation of sodium sulphate, according to the equation:



Fort (*J. Soc. Chem. Ind.*, 1916, 35, 305) supported his theory also by experiments carried out with inorganic bases instead of the complex wool-substance. The colour acid of Crystal Scarlet has little or no action on magnesium oxide suspended in cold water, but if magnesium sulphate is added, the magnesium salt of the dye acid is formed almost quantitatively, and free sulphuric acid is found in the solution. Similarly, the sodium salt of Crystal Scarlet does not react with magnesium oxide, but on the addition of sulphuric acid, with consequent formation of magnesium sulphate, double decomposition takes place, with formation of the magnesium salt of the dye acid, in a similar manner to that explained above for wool:



With some dyestuffs it is easy to obtain level colours, but with others it is difficult. Acid Orange GG, for example, dyes wool evenly, whilst others, such as polar yellows, tend to give unlevel results unless used very carefully. Speakman (*J. Soc. Dyers Col.*, 1934, 50, 349) found that levelling properties are determined mainly by the colloidal character of the dyestuff in solution. Other things being equal, the tendency of a dyestuff to become colloidal in the acid bath increases with the molecular weight of the organic nucleus, and decreases with the degree of sulphonation. Such things as the relative positions of azo and sulphonic groups are of importance also. Goodall (*J. Soc. Dyers Col.*, 1938, 54, 45) recommended the entering of goods into the dye-bath at a high temperature ( $100^\circ \text{C}.$ ) without sodium sulphate in the case of truly colloidal dyestuffs with pronounced unlevel dyeing properties, which is the exact opposite of the method generally adopted.

**Subdivisions of the Acid Dyes.**—Although the acid dyes owe their name to the fact that they are generally used in an acid bath, they do not all require acid as an assistant, nor in some cases an acid so strong as sulphuric acid. From the dyer's point of view they may be subdivided into—

- (1) Those which require a comparatively strong acid.
- (2) Those which will dye in a faintly acid bath, or in the presence of a weak acid.
- (3) Those which will dye in a neutral or even faintly alkaline bath.

The first class contains most of the common acid dyes, which are used with 4 to 5 per cent. of sulphuric acid or a larger quantity (8 to 10 per cent.) of a weaker acid, such as formic or acetic. Sometimes, instead of using sulphuric acid and sodium sulphate, sodium bisulphate is added alone. This, when dissolved in water, gives sodium sulphate and sulphuric acid:

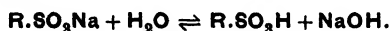


About 10 per cent. of bisulphate ( $\text{NaHSO}_4$ ) is necessary to give 4 per cent. of sulphuric acid.

The second class includes such dyes as the eosines and the sulphon-cyanines.

In some cases (e.g. sulphon-cyanines) the dye acid is only slightly soluble in water, and hence the acidity of the bath must be developed gradually, either by the cautious addition of a weak acid or by the use of ammonium acetate, which will be described later.

The third class contains such dyes as Alkali Blue, Alkali Violet, Neutral Blue and Burl Black. It has been suggested that these three groups are determined by the readiness with which the dyestuff is hydrolysed by water. The members of the third group are hydrolysed readily into the dye acid and sodium hydroxide:



When using dyestuffs of the second class, a little sulphuric acid is added to the bath towards the end of the dyeing to assist exhaustion. This may be done also when a neutral bath is used. The alkali blues are dyed in a slightly alkaline bath containing about 1 per cent. of borax, then rinsed, and passed into a bath containing hot dilute sulphuric acid to develop the colour. The neutral-dyeing acid dyestuffs are useful for tinting wool when dyeing wool-cotton mixtures.

**Fastness of Acid Dyes.**—The term *fastness* means the power which a dye has of withstanding such processes as exposure to light and washing. The type of fastness required depends upon the purpose for which a dyed fabric is used. Thus, in the case of goods to be used for a garment which will always be exposed to light, but never washed, fastness to light is very important, but fastness to washing does not matter. On the other hand, with dyed under-clothing, fastness to washing or perspiration is of more importance than fastness to light. Dyestuffs have to be chosen with regard to the particular tests which they are required to pass. The more common are fastness to (i) light, (ii) washing, (iii) milling, (iv) acids, (v) alkalis, and (vi) stoving. The methods used in testing fastness will be described later. Very few dyes are fast to everything, but many will pass one or two of the tests while failing in others. This is the case with the acid dyes. Their fastness varies very much. For example, Acid Magenta is fast to acids but to nothing else. Ponceau RG is fast to both acids and stoving, but only moderate in other particulars. Fast Acid Blue RH is fast to light, acids, and alkalis, but not to stoving. Coomassie Navy Blue will stand milling, is fairly fast to light and alkalis, less fast to acids, but not fast to stoving. As a class, the acid dyes may be regarded, with exceptions, as being fairly fast, though as a rule they are not very fast to the action of alkalis. They may in many cases be entirely stripped from the fabric by boiling it with a dilute solution of ammonia or sodium carbonate.

### Application of the Acid Dyes to Wool.

The acid dyes are used very extensively for wool. All-wool fabrics are always dyed with them, except when really fast colours are required. In such cases mordant dyes, vat dyes, or aniline black are used. Acid dyes are used also for mixtures of wool and silk, since they dye both fibres directly, but are not so suitable for unions (wool and cotton), as they have no affinity for unmordanted cotton. They are used, however, when it is desired to leave cotton threads white.

**Preparation of Woollen Goods.**—Woollen goods are always scoured before dyeing by the methods already described. For light colours or bright shades, bleaching is sometimes necessary also. The increased affinity of wool which already contains acid for the acid dyes has been mentioned. But if wool is

treated with sulphuric acid and dried or exposed to light without washing out the acid, it has a greatly decreased affinity. This is the cause of considerable trouble in dyeing carbonized wool. Goods which have been carbonized should be freed carefully from acid before dyeing. Stoved wool is always liable to contain sulphur dioxide. In order to remove acid, the goods are soaked in a dilute (1 per cent.) solution of sodium carbonate or ammonia, and then washed thoroughly with water. Potassium permanganate may also be used to remove sulphurous acid. The goods are placed in a bath of water, and a dilute solution of permanganate is stirred in slowly till a faint pink colour is imparted to the water. They are then washed thoroughly with water.

**Dissolving Acid Dyes.**—The acid dyes are relatively easy to dissolve compared with members of some of the other classes. Nevertheless, certain precautions should be taken in dissolving them. The requisite amount of dyestuff is mixed into a smooth paste with cold water, and then sufficient boiling water is added to dissolve it completely. Distilled or condensed water is preferable, but if it is not available the temporary hardness may be corrected with a little acetic acid. It is advisable to strain the solution through calico before allowing it to enter the dye-bath, in order to remove any undissolved particles of dye.

**Preparing the Dye-bath.**—The quantity of dyestuff to be used depends upon the shade of colour required. From 0.5 to 5 per cent. is dissolved and added to the bath, which should contain sufficient water to allow the goods to be worked comfortably. From twenty to fifty times the weight of the material will be required, according to the nature of the goods. (*N.B.*—1 gallon of water weighs 10 lb.) Next, from 10 to 25 per cent. of Glauber's salt is added, followed by from 1 to 5 per cent. of sulphuric acid. The quantities of Glauber's salt and acid depend naturally upon the amount of dyestuff used. For 0.5 per cent. of dyestuff, 10 per cent. of Glauber's salt and 1 per cent. of sulphuric acid would be sufficient, these being gradually increased to the maxima with increasing percentages of the dyestuff. It should be noted here that whenever percentages of dyestuffs or assistants are stated, it always means that they are calculated on the weight of material to be dyed.

**General Method of Dyeing.**—The dye-bath is now heated to a temperature of 140° F. (60° C.). The goods are wetted out with water at the same temperature, and entered. Dry goods are never put into a dye liquor. This would cause the dye to be rapidly absorbed at the surface, and would result in uneven dyeing. After the goods have been introduced, the temperature of the bath is raised gradually to the boiling-point. This should take about half an hour. The bath is kept just at the boiling-point for from half an hour to an hour. The goods are turned or stirred occasionally, to ensure equal distribution of the dye liquor. The somewhat prolonged boiling of the bath aids in the level deposition of the dye, possibly by tending to dissolve it from the surface and deposit it in the interior of the fibre. In fact, if at the end of the dyeing the colour does not appear quite even, the goods should be put back into the bath, and the boiling continued for a further fifteen or thirty minutes. When the dyeing is complete, the goods are rinsed, hydro-extracted, and dried. The bath should be nearly exhausted. Soft water is not absolutely essential for acid dyestuffs. But if hard or artificially softened water is used, the alkalinity should be neutralized with dilute sulphuric or acetic acid before making up the bath.

**Effect of Temperature.**—Wool has practically no affinity for acid dyes at low temperatures. The affinity becomes marked only at about 140° F. (60° C.). From this temperature it increases up to the boiling-point, where

it attains its maximum. This is the reason why the temperature of the dye-bath must not be raised too quickly to the boiling-point. The increase in affinity of the wool for the dyestuff should be developed gradually and evenly, and not by jumps. Rapid dyeing is often bad dyeing, and, conversely, slow dyeing is good.

**Variations of the General Method.**—The method just described is a general one, and is varied in detail by different dyers. As mentioned already, sodium bisulphate may replace Glauber's salt and sulphuric acid. It is, as we have seen, a mistake to suppose that sulphuric acid does not damage wool. It has been shown that it does, but wool has a large reserve of tensile strength to draw upon. There is, however, much less danger of damage if a weaker acid, such as formic, is substituted for sulphuric, and this is sometimes done. Sometimes the bath is made up with the dyestuff and sodium sulphate. The goods are then boiled gently in this for a quarter of an hour before adding the acid. This enables the dye liquor to penetrate the goods more thoroughly before its dyeing action is developed. If this method is adopted, the acid should be added in portions at intervals of about fifteen minutes, or the dyeing may be too rapid. Sometimes the goods are put straight into a boiling bath. This is possible with a dye known to be a good, level dyer, but with others it may cause uneven results.

According to Rendell and Thomas (*J. Soc. Dyers Col.*, 1935, 51, 157), turbulent conditions in the dye-bath promote rapid and complete penetration and exhaustion. The application of air-bubbling through the dye liquor is a powerful aid to exhaustion. An apparatus by which this effect can be obtained is described.

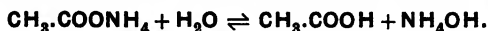
*Dyes which tend to give Uneven Colours.*—Dyestuffs vary in the quality of even dyeing. With some it is quite easy to get good results, but with others more difficult. If a dyestuff is known or found to be one which is liable to give uneven colours, the general method must be varied to suit it. The object in view is to develop the dyeing action slowly and regularly, since uneven shades are caused generally by too rapid absorption of the dye. Since it is the dye acid which is the actual dyeing constituent of the dyestuff, this means that its liberation in the dye-bath must be retarded, and this can be done by adding the acid very gradually, instead of all at once at the beginning of the operation.

The practice usually adopted is to divide the sulphuric acid into three portions. One portion is added to the bath at once, and the other two are added at intervals of about half an hour during the dyeing operation. When the acid is added, the goods should, if practicable, be lifted out of the dye-bath, and before they are replaced the liquor should be stirred, in order to make certain that the acid is evenly distributed. The action of acids in the acid dye-bath is proportional to their pH-value, and therefore acetic acid is a far less energetic agent than sulphuric acid, while formic acid is intermediate between the two. Should there be a strong affinity between the fibre and the dye, a better result will be obtained by using acetic or formic acid in place of sulphuric acid. With unlevel dyes, the acetic acid should be added in three parts in the manner just described. If the bath will not exhaust satisfactorily with acetic acid, one may dye as far as possible with it and, finally, complete the exhaustion by adding about one per cent. of sulphuric acid diluted with water. The following method is recommended by the British Dyestuffs Corporation:—

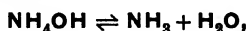
Commence dyeing with 10 to 15 per cent. of Glauber's salt and 2 to 5 per cent. of acetic acid. After boiling for from a half to three-quarters of an hour, exhaust the dye-bath by the careful addition of either from 1 to 3 per cent. of

acetic acid or up to 1 per cent. of sulphuric acid, well diluted with water in either case.

There is, however, another method of gradually adding acid to a dye-bath. Ammonium salts are hydrolysed into ammonium hydroxide and the acid. This is illustrated by the equation (using ammonium acetate as an example):



The ammonium hydroxide in boiling water is decomposed into ammonia and water, according to the equation:



and the free ammonia comes off in the steam. In this way the ammonia is gradually removed, and so, since the hydrolysis is reversible, the whole of the acid of the ammonium salt is gradually liberated. It is obvious that this method of adding the acid is superior to that described above, for the process is both continuous and gradual. Ammonium acetate may be made when required by adding acetic acid to a solution of ammonia till a neutral or very faintly acid reaction is given by litmus-paper. Ammonium sulphate or formate can be used in the same way, but are not so readily decomposed as ammonium acetate. In practice, from 1 to 4 per cent. of ammonium acetate together with from 15 to 25 per cent. of Glauber's salt is used. After dyeing at the boiling-point for half an hour, from 1 to 2 per cent. of diluted acetic acid is added, and the boiling continued to exhaust the bath.

When using an acid dye with which one is not familiar, it is wise to dye first without any acid. If the fabric becomes dyed, then the use of ammonium acetate is indicated, with a little acetic acid at the end. If the fabric is not dyed, either acetic, formic, or sulphuric acid may be used, remembering that acetic acid is safer, and that the exhaustion can always be completed by adding about 1 per cent. of sulphuric acid towards the end of the operation.

*Dyeing with Acetic Acid.*—When using dyestuffs belonging to the second class, the process is exactly the same, except that acetic acid is used instead of sulphuric acid, and from 1 to 2 per cent. of sulphuric acid may be added (well diluted with water) towards the end of the dyeing to assist exhaustion. Practically all the acid dyestuffs can be used for pale shades with acetic acid alone, bright colours being obtained.

*Neutral-dyeing Acid Dyestuffs.*—The dye-bath is made up with Glauber's salt and dyestuff. Dyeing is carried out in the usual manner, except that from 1 to 2 per cent. of acetic acid may be added towards the end of the process to promote exhaustion.

For particulars of the recently developed technique of high-temperature dyeing, see p. 527.

**Special Methods.**—A few of the acid dyes require special methods of application. That for the alkali blues and violets has been described above.

*The Phthaleins, or Eosine dyes,* include the various Eosines and Phloxines, and Rose Bengal. These dyes are applied in a slightly acid bath which contains, as well as the requisite amount of dyestuff, 2 lb. of cream of tartar, 2 lb. of alum, and 1 to 2 lb. of acetic acid of 9° Tw. for every 100 lb. of wool to be dyed. The wetted-out goods are entered, the bath is slowly raised to the boil, and the goods are then dyed at the boil for half an hour. Provided the liquor is heated slowly, even shades can be obtained. Sulphuric acid or sodium bisulphate should never be added to the bath, for they make the shades duller.

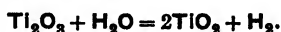
*The Sulphon-cyanines,* of which Coomassie Navy Blue is an example, are much used for wool. The dye acid is not very soluble in water, and hence



excess of acid must be avoided. They dye wool in a neutral bath or one containing ammonium acetate, the method described above being employed. These dyes are, however, sensitive to reducing agents, and, to prevent any danger of reduction, 1 per cent. of potassium dichromate is frequently added to the bath. This does not affect the colour.

**Levelling of Uneven Shades.**—Unevenly dyed goods may be due to some fault in the material itself or to want of care in dyeing. If oil, calcium or magnesium soaps, or other bodies are present in the goods, which prevent the dye liquor from penetrating, it is very difficult to get even results, unless these impurities are removed first. Uneven shades, due to the dyeing itself, may be treated in the following manner: The simplest thing to do is to put the goods back into the bath and boil them gently again for about fifteen minutes. This tends to redissolve the dye from the surface and redeposit it more evenly. Sodium sulphate in moderately dilute solutions acts as a levelling agent. Concentrated solutions not only prevent the dye from being deposited, but redissolve (or strip) any acid dye which is present on the goods. Badly dyed goods may be partly stripped by boiling them in a solution of sodium sulphate containing from 30 to 40 per cent. of the salt, and then redyed. Many of the acid dyes are stripped by boiling gently with a dilute solution (about 1 per cent.) of ammonia or sodium carbonate. If the goods are stripped by means of ammonia, they can be redyed in the same bath by nearly neutralizing the ammonia with dilute acetic acid, adding sodium sulphate, and boiling gently. In this way waste of dyestuff may be avoided. If these methods are not successful, more powerful stripping agents must be employed, and, after stripping and washing, the goods dyed again in a fresh bath.

**Stripping Agents.**—These are, in general, either reducing or oxidizing agents. The former are less powerful in their action than the latter, and also not so likely to damage the fibre. The chief stripping agents are (i) sodium hydrosulphite; (ii) condensation compounds of formaldehyde with sulphurous acid, such as *decrolein* and *formosul*; (iii) titanous chloride; (iv) dilute solutions of bleaching powder; and (v) potassium dichromate and sulphuric acid. Sodium hydrosulphite and decrolein are described in Chapter XVII. They are used in the following way: To strip with hydrosulphite, about 3 per cent. on the weight of the goods is dissolved in a bath of cold water, and the dyed goods are worked in the cold or warm bath. Decrolein and formosul require the addition of an acid to develop their reducing action, and are also comparatively stable at low temperatures. From 3 to 5 per cent. of the substance is dissolved in cold water, and about the same quantity of acetic acid is added. The goods are then put into the cold bath, and the temperature is raised slowly nearly to the boiling-point. Titanous chloride,  $\text{TiCl}_3$ , may be used in a cold aqueous solution, yet although it is a powerful reducing agent, it is not employed extensively. It will often strip colours which cannot be removed by any other reducing agent. It is a derivative of titanium sesquioxide,  $\text{Ti}_2\text{O}_3$ . This compound reacts with water, giving titanium dioxide and hydrogen:



All of the stripping agents mentioned hitherto are reducing agents, and are always to be preferred to oxidizing agents. Among the chief oxidizing stripping agents is bleaching powder, which is used in an aqueous solution at a concentration not exceeding 1 gram per litre. This may be made by diluting a solution of 1° Tw. density with approximately twice its volume of water. The dyed goods are soaked in the cold solution, then washed with water,

soured in a dilute solution of acetic acid, and again washed. Bleaching powder solution is not suitable for animal fibres, since they are readily attacked by it with the formation of chloramines. A mixture of sodium dichromate and sulphuric or acetic acid is the most powerful stripping agent known. About 3 per cent. of dichromate and 2 to 3 per cent. of acetic acid may be used. The goods are started in a cold bath, and the temperature is raised gradually to the boiling-point. They are then washed thoroughly. This method is only used when others fail, since it is liable to damage the wool fibre, and also to mordant it, thus altering its affinity for dyes. Sodium dichromate is decomposed by sulphuric acid in the presence of oxidizable bodies in accordance with the equation:



Whatever stripping agent is employed, the goods must be very thoroughly washed before reyeing. The last traces of acid must be neutralized by means of a bath of dilute ammonia or sodium carbonate. If this is not done, the goods will have an abnormal affinity for acid dyestuffs, and dye irregularly. Different classes of dyestuffs act differently with stripping agents. Small patterns of the material are tested, and the method found to be most satisfactory is applied to the bulk.

**Acid Chrome Dyestuffs.**—This group includes (i) the chromotrope dyestuffs, derived from chromotropic acid; and (ii) acid chrome, acid mordant, or after-chromed acid dyestuffs of varying composition.

As explained above, they contain hydroxyl groups characteristic of the mordant class, and can act both as acid and as mordant dyestuffs. They are often grouped with the latter, but as they are used almost exclusively for wool it is more convenient to deal with them as acid dyestuffs. Dyestuffs containing the mordant hydroxyl group can be distinguished by the fact that they give a precipitate when heated with the *chromium-fluoride reagent*. This consists of a solution of 10 g. of chromium fluoride and 5 g. of sodium acetate in 100 ml. of water.

Acid mordant and ordinary acid dyestuffs may be distinguished by dyeing small pieces of wool mordanted with chromium oxide, and unmordanted wool, with the dyestuff in a bath made acid with formic acid, and then comparing the colours and fastness of the dyed samples. Acid chrome colours, when dyed on a mordant, are much faster to a boiling 1 per cent. solution of ammonia than ordinary acid colours, and commonly have a different colour or shade.

*The Chromotrope Dyes*, when used as acid dyes, generally give red colours, which are changed to blue or black by chroming. These blues and blacks are much faster than those of ordinary acid dyes. The dyeing may be carried out in the following way: The dye-bath is made up with 4 per cent. of sulphuric acid and 20 to 25 per cent. of Glauber's salt, as for an ordinary acid dyestuff, and the goods are entered at 140° F. (60° C.), and dyed as usual. They are then lifted, and from 0.5 to 2 per cent. of potassium dichromate dissolved in water, together with 1 per cent. of sulphuric acid, is added to the bath, after which the goods are returned, and boiled gently for a further three-quarters of an hour.

*The Acid Chrome Dyestuffs* do not, as a rule, give useful colours when dyed directly on wool from an acid bath, differing in this respect from the chromotropes. But when they are after-chromed, good, though frequently different, colours are produced. These are often fast to milling, and are, therefore, useful for dyeing woollen cloths. They cannot be used for silk, since potassium dichromate and sulphuric or acetic acids rapidly damage the fibre.

The acid chrome colours are dyed in much the same way as the chromotropes. The dye-bath is made up with from 1 to 5 per cent. of dyestuff, 10 to 25 per cent. of Glauber's salt, and 1 to 5 per cent. of acetic acid. The goods are wetted out, and entered at 140° F. (60° C.); the temperature of the bath is then raised slowly to the boiling-point, and the liquor kept gently boiling for about three-quarters of an hour. The bath is then allowed to cool off for a short time, after which the goods are lifted, and from 0.5 to 2 per cent. of potassium dichromate is added, depending upon the percentage of dyestuff used. The goods are then returned to the bath, and the contents of the latter boiled gently for a further forty-five minutes, after which they are washed and dried. In order to obtain good results it is important to observe the following points:—

(1) The dichromate should not be added till the dye-bath is very nearly exhausted. If it is added too soon, the dyestuff will be precipitated in the bath, and cannot then be taken up by the fabric. It may also become attached loosely to the surface of the fibres, and give colours which "rub."

(2) The dichromate must not be added to the boiling dye-bath, but at a temperature of about 140° F. (60° C.).

(3) The goods must be lifted before adding the mordant.

(4) Excess of dichromate must be avoided, as it may alter the colour, and even damage the wool. For this reason the goods, after dyeing, should never be left in contact with the hot liquor, but should be washed off at once.

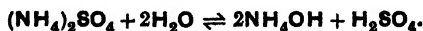
**Metachrome or Monochrome Colours.**—These are not acid, but mordant dyestuffs. It will, however, be convenient to notice them here, since the method of using them may be employed also for many of the true acid mordant colours. The metachrome dyestuffs are used in the following manner:—

The requisite percentage of the dyestuff is dissolved in the bath together with the Glauber's salt. The potassium dichromate (from 0.5 to 2 per cent. according to the percentage of dyestuff used) is dissolved in water in a separate vessel, and to this is added from 1.5 to 5 per cent. of ammonium sulphate, previously dissolved in water and made alkaline with ammonia. As a general rule, half as much dichromate as dyestuff is used, and 2.5 times as much ammonium sulphate as dichromate. This mixture is added to the dye-bath, which is then heated to 140° F. (60° C.), and, after the goods have been entered, raised to the boiling-point for about an hour.

Potassium dichromate in the presence of ammonium hydroxide is changed into potassium and ammonium chromates, in accordance with the equation:

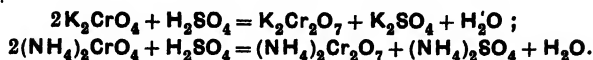


Now chromates do not act as mordants for these dyestuffs. But when the dye-bath is boiled, the free ammonia is expelled. After this has taken place, the ammonium sulphate is gradually hydrolysed into ammonium hydroxide and sulphuric acid:



The ammonium hydroxide is decomposed, at the temperature of the bath, into volatile ammonia and water. As the ammonia is volatilized with the steam, the quantity of free sulphuric acid in the bath increases gradually. This produces the conditions necessary for the dyestuff to dye the wool directly in its capacity of an acid dye. But it also does something else. The chromates of potassium and ammonium present in the solution are reconverted by the

sulphuric acid into potassium and ammonium dichromates, as shown by the equations:



As soon as dichromate is present, it reacts with the mordant groupings of the dyestuff, already on the fibre, and forms an insoluble colour lake; in this way the dyeing and mordanting proceed together, and no after-chroming is necessary. But the addition of a little acid to the bath may be required towards the end of the dyeing to complete the reconversion of the chromate to dichromate, and generally to assist exhaustion.

**Neolan Dyestuffs.**—These are characterized by the use of a large quantity of sulphuric acid, viz. 6 per cent. (168° Tw.) for light shades and 8 per cent. (168° Tw.) for dark shades. Ten per cent. of Glauber's salt is used also. The dye-bath is prepared with half of the sulphuric acid. The dissolved dyestuff is sieved in, and dyeing begun at 100° to 120° F. (37·8° to 48·9° C.). The temperature is raised to the boiling-point in 30 min., after which the rest of the acid is added, and boiling is then continued for 45 min. The dyed goods are washed with water, a little ammonia being used in the last washings to free the goods from acid.

### Application of the Acid Dyes to Silk.

Although silk can be dyed directly with the acid dyes, the colours are not so fast as those on wool, and in some cases can be removed by washing with water alone. The dyeing of silk differs from that of wool in certain important particulars. We have seen that wool has little affinity for dyes at a low temperature. Silk, on the other hand, can be dyed in a lukewarm or even cold bath. As a rule, its maximum affinity is developed between 140° and 180° F. (60° and 82·2° C.). At temperatures above 180° F. (82·2° C.) the affinity decreases gradually, till at the boiling-point it is so small that with some acid dyes silk is not dyed at all. This effect is more marked in the presence of a slight excess of acid. It is of interest to note in this connection that Harrison and Gee found that silk develops its maximum electrical charge at 180° F. (82·2° C.). This difference between wool and silk may be illustrated by the following experiments. Some wool and some silk yarn are plaited together. Equal weights are then dyed in separate dye-pots with 2 per cent. of acid magenta and 3 to 5 per cent. of acetic acid. One is dyed at the boiling-point, and the other at about 100° F. (37·8° C.). In the first case the wool will be dyed, and the silk undyed; while in the second the dye is taken up almost entirely by the silk, the wool remaining nearly white.

**Two-colour effects** on mixtures of wool and silk may be produced by first dyeing the silk at a low temperature with an acid dye which will not dye the wool under these conditions, and then dyeing the wool in a boiling bath with acetic acid and an acid dye which will not dye the silk. Not all of the acid dyes can be used: they may, in fact, be classified according to their selective action on wool and silk.

**Effect of Boiling Water on Silk.**—Apart from the fact that silk develops its maximum affinity for dyes at about 180° F. (82·2° C.), there are other reasons why the dye-bath should not be boiled. When silk is boiled with water, its tensile strength and lustre are affected deleteriously. There is some danger also of rupturing the fibres. Finally, in the case of skeins the threads are liable to become entangled.

**Use of Assistants.**—Glauber's salt is not suitable for use with silk as it diminishes its lustre. Boiled-off liquor obtained in degumming silk (or bast soap) is used instead. This is a colloidal solution which acts as a good levelling agent. It has also another advantage in the case of raw silk, namely, that it prevents undue loss of silk-gum during the dyeing process. A solution of glue can be used in the same way. Boiled-off silk may be dyed without any assistant. Sulphuric acid also damages the silk fibre. If acid is used, it should be acetic. Since boiled-off liquor contains dissolved soap, excess of acid would liberate fatty acids, and destroy the value of the liquor. Hence the bath must be neutral or only very faintly acid. This has the effect of making it necessary to use only those acid dyes which will dye in a neutral or faintly acid bath. This does not, of course, hold when no boiled-off liquor is present, but in the absence of such it is rather difficult to get even shades.

**General Method for Silk.**—From 10 to 15 gallons of boiled-off liquor are used for 10 lb. of silk, diluted with soft water. The boiled-off liquor should be about 25 per cent. of the bath. Hard water causes the precipitation of calcium and magnesium soaps, which stick to the silk, and render it impervious. Dilute acetic acid is stirred into the liquor until it has a very faint acid reaction to litmus-paper. This is to neutralize any alkali that may be present. The bath is next warmed to about 100° F. (37·8° C.), and any scum or fatty acid which rises to the surface is skimmed off. This operation is termed *breaking the liquor*. The silk is wetted down in the bath and then removed, and the solution of the dyestuff is added. The silk is then entered, and the temperature is raised slowly to about 190° F. (87·8° C.), the goods being turned frequently. After dyeing for from 30 to 45 min. at 190° F. (87·8° C.), the silk is removed and rinsed. The bath should not be allowed to boil. Silk is very commonly dyed in hanks, which are hung on smooth bent rods and allowed to dip into the dye liquor, the hanks being turned from time to time to ensure that every part gets the same treatment. Better results are obtained if, instead of adding the dye to the bath all at once, it is divided into three portions and added at intervals. In this case the first third of the dye is added at about 100° F. (37·8° C.). The silk is worked in this for about fifteen minutes. The second third is then added, and the temperature raised to about 140° F. (60·0° C.). After dyeing at this temperature for fifteen minutes, the remaining third is added, and the temperature raised to 190° F. (87·8° C.).

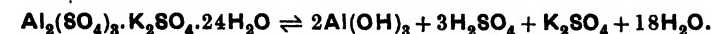
If scroop is required, the silk, after rinsing, is soaked in a dilute solution (0·5 per cent.) of acetic or tartaric acid. It is then squeezed and dried without washing.

### Application of the Acid Dyes to Cotton.

The acid dyes have no direct affinity for cotton, and will dye it only after it has been mordanted with a basic metallic oxide. The colours, even then, are not fast to washing; but, owing to their fastness to light, they are used where this quality, and not fastness to washing, is required. Such cases are cotton upholstery. Unmordanted cotton is occasionally stained with acid dyes, that is to say, the cotton is soaked in as short a bath of the dye as possible, and squeezed and dried without washing. It is usual in such cases to add enough salt to the bath to bring its density up to 5° to 7° Tw. Light shades, which are fast to light but not to washing, are obtained in this way.

**Mordanting Cotton.**—A solution of alum or basic aluminium sulphate is the commonest mordant for cotton, and occasionally a solution of the salt alone is used. When an aqueous solution of alum is boiled, it becomes hydrolysed,

with the formation of aluminium hydroxide, which becomes attached to the fibre:



The bath is made up with the dye, the least amount of water possible, 10 to 20 per cent. of alum, and 20 per cent. of Glauber's salt. The wetted-out cotton is entered, and dyed at 180° F. (82.2° C.) for an hour. The mordanting and dyeing operations are carried out simultaneously in the same bath in this way. At the end of the hour the goods are squeezed and dried without washing. The amount of hydrolysis which takes place when a solution of alum is boiled is very limited. When, however, a solution of a basic sulphate of aluminium is either boiled or diluted, a more basic and less soluble salt is produced. In this way much more aluminium hydroxide can be deposited on the fibre than is possible from a solution of the normal salt. Thus, while a boiling 20 per cent. solution of normal aluminium sulphate gives up 13 per cent. of alumina to cotton, a solution of the basic salt  $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$  will, under the same conditions, give nearly 50 per cent. The basic salt  $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2$  is generally used. It is only slowly decomposed by boiling, and gives up about 50 per cent. of alumina to the cotton. The decomposition is assisted by the presence of dissolved sodium sulphate. This basic salt is obtained when aluminium sulphate or alum is treated with sodium carbonate in the proportions required by the equation:



If crystalline aluminium sulphate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , is used, 666 parts will require 106 of dry sodium carbonate, i.e. 100 will require 16. A solution containing these proportions is made, and its specific gravity adjusted to about 10° Tw. The cotton is worked or soaked in this solution, wrung out, and dyed without washing. Or, after soaking in the mordant, it is dried at a low temperature, and then passed into a cold bath of dilute ammonia for ten minutes. It is then wrung out, washed, and is ready for dyeing. The drying and treatment with ammonia complete the precipitation of the alumina.

**Aluminium Hydroxide fixed on Tannic Acid.**—Colours somewhat faster to washing may be obtained by impregnating the cotton with tannic acid, then mordanting it with alum or aluminium acetate, and finally dyeing it in the usual way. The cotton is worked for a short time in a boiling bath containing 4 per cent. of tannic acid; it is then allowed to stand in the cooling bath for two hours, and at the end of this period it is transferred to a bath of alum and soda or aluminium acetate. The aluminium hydroxide combines with the tannic acid to form a basic tannate of aluminium. The mordanted goods are dyed in the usual way in a bath containing the necessary amount of dyestuff and 20 per cent. of Glauber's salt.

**Dyeing with Sodium Stannate and Alum.**—This method gives specially bright shades with acid dyes, but suffers from the disadvantage of giving the yarn a harsh feel. The cotton is worked for half an hour in a bath containing 4 oz. of sodium stannate per gallon of water. It is then left to soak in the bath for several hours, and after this is wrung out and transferred to another bath, which contains 20 lb. of alum and 3 lb. of calcined soda (or 6 lb. of crystal soda) per 100 gallons of water. After this treatment the goods are wrung out, and dyed in a bath containing the requisite amount of dye.

**Staining Cotton with Acid Dyes of the Eosine Group.**—These dyes give a colour which lacks fastness to light and washing, but when delicacy of shade alone is desired they may be used. The dye-bath must be as short as possible, and 10 per cent. of dye must be used to give a full shade. Common salt helps to

fix the dye, and 1 lb. should be added for every 2 gallons of water. The cotton is usually dyed between 100° and 140° F. (37·8° and 60° C.), and the goods should not be handled with wet hands, for this will give lighter patches where handling has occurred. The dyeing takes from 30 to 45 min., and at the end the goods are hydro-extracted without washing, and dried. Eosine, Phloxine, and Rose Bengal are the more important dyes which are applied in this way.

### Tests for Fastness of Dyestuffs.

It will be convenient to describe here the more important tests for fastness which are applied to dyed fabrics. Those used for a particular sample differ according to the requirements. There are degrees of fastness to each test, which may be designated by the adjectives: good, fair, moderate, poor, and bad. The tests used are (i) general to all fibres; and (ii) applicable to special fibres.

**General Tests.**—(1) *Fastness to Light*.—One-half of a rectangular piece of the dyed fabric is covered by means of two pieces of cardboard, one on each side, fastened together by means of clips. The uncovered part is then exposed to a south light, and compared at intervals, up to the end of a month, with the covered portion, and any alteration in shade is noted. If there is no perceptible change in a month the fastness is good.

(2) *Fastness to Washing*.—A solution of 2 g. of soap and 0·5 g. of sodium carbonate in a litre of distilled water is used. The sample is worked gently in some of this solution for 15 min. at a temperature of about 140° F. (60° C.) for wool or silk and at the boiling-point for cotton. It is then washed in distilled water, dried, and compared with the original fabric.

(3) *Fastness to Rubbing*.—A piece of the dyed fabric is rubbed on a piece of white cotton, linen, or paper.

(4) *Fastness to Perspiration*.—A piece of the sample is soaked for twenty-four hours in an artificial perspiration made by dissolving 1 g. of lactic acid and 1 g. of salt in 100 ml. of water. It is then rinsed with distilled water, dried, and compared with the original pattern.

(5) *Fastness to Acids and Alkalis*.—The sample is spotted with a 5 per cent. solution of the acid or alkali whose action it is desired to test, and any alteration is noted.

(6) *Fastness to Ironing*.—A sample is damped, and ironed with an ordinary flat-iron.

The report of the Fastness Committee of the Society of Dyers and Colourists (1934) gives a full account of methods of testing for fastness to light, washing, and perspiration.

**Special Tests for Wool.**—(1) *Fastness to Milling*.—A piece of the material is boiled in a 1 per cent. solution of soap containing also 0·5 per cent. of sodium carbonate. At intervals it is taken out, and rubbed between the hands or pounded with a pestle and mortar.

(2) *Fastness to Stoving*.—A bell-jar, or large, wide-mouthed, stoppered bottle, is filled with sulphur dioxide. A piece of the sample is moistened with water, and left suspended in the jar overnight. It is then washed, dried, and compared with the original.

(3) *Fastness to Decatizing and Potting*.—It is very difficult to carry out these tests satisfactorily in a laboratory. Decatizing may be simulated by wrapping a piece of the fabric round a small circular metal tube pierced with holes and then wrapping tightly over this some other material, such as calico. The ends of the tube are provided with corks through which small glass tubes

are passed, thus making a chamber through which a rapid current of steam can be passed. Fastness to potting may be tested by boiling a piece of the fabric in a flask connected with a reflux condenser for several hours.

(4) *Fastness to Carbonizing*.—A sample is impregnated with a 5 per cent. solution of sulphuric acid, dried at a low temperature, and then heated for an hour to 80° C. It is then washed with water, weak sodium carbonate solution, and finally with water. It is then dried, and compared with the pattern.

**Special Tests for Cotton.**—(1) *Fastness to Bleaching*.—A portion of the sample is soaked for one hour in a clear solution of bleaching powder of 1° Tw. strength. It is then washed with water, soured in dilute acetic acid, washed again, and dried.

(2) *Bleeding Test*.—A piece of the dyed sample is boiled, together with a piece of undyed mercerized cotton, in water or a 0.5 per cent. solution of soap. In the absence of bleeding the undyed piece remains white.

(3) *Fastness to Cross-dyeing*.—The sample is boiled for three-quarters of an hour in a bath made up exactly as for an acid dyestuff, but omitting the dye. That is, it should contain 4 per cent. of sulphuric acid and about 20 per cent. of Glauber's salt. The sample is then washed, dried, and compared with the pattern.



## CHAPTER XXVI.

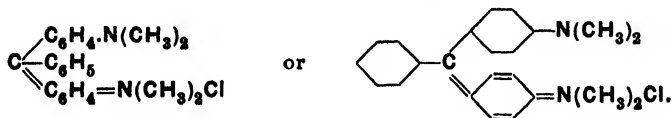
### THE BASIC DYESTUFFS.

From the historical point of view the basic dyestuffs are of great interest, since Perkin's mauve (Chapter I), the first synthetic dye, is a member of this class. Magenta, Methylene Blue, Malachite Green, which were prepared soon afterwards, are also basic dyes.

**Chemical Nature of Basic Dyestuffs.**—The class owes its name to the fact that every member of it is a salt of an organic base. These contain an amino ( $\text{NH}_2$ ) group or a substituted amino group. In the latter, either one or both hydrogen atoms are replaced by an organic radical, such as  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_6\text{H}_5$ . The basic dyestuffs are in most cases hydrochlorides of the dye base, but some are oxalates or double salts with zinc chloride. The dye base which it contains is the actual dye and not the dyestuff itself.

**Classification of Basic Dyes.**—The basic dyes are very numerous and of varied chemical structure. They may, however, be divided, according to Cain and Thorpe (*The Synthetic Dyestuffs*), into certain groups, including the following:—

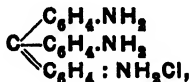
(1) *Derivatives of Triphenylmethane*,  $\text{CH}(\text{C}_6\text{H}_5)_3$ .—Among these is Malachite Green,



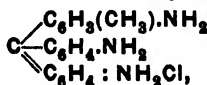
It should be noted that this dyestuff contains a para-quinonoid grouping,



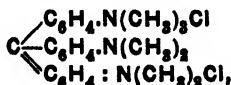
as the chromophore. This is characteristic of this class of dyestuffs. Para-rosaniline hydrochloride,



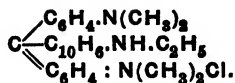
and rosaniline hydrochloride,



the principal constituents of magenta, are also triphenylmethane derivatives, together with many others, such as Methyl Green,



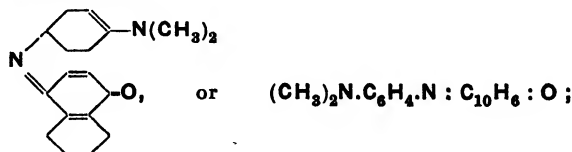
and Victoria Blue R,



In all of these the para-quinone grouping is present.

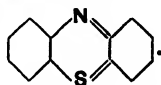
(2) *Diphenylamine dyes*, derivatives of diphenylamine,  $\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ .—This group is divided into several sub-groups:

(a) *The Indophenols*, which are comparatively simple substances. Indophenol white (DH), used as a vat dyestuff, is an example. It is made from *p*-nitroso-dimethylaniline hydrochloride and  $\alpha$ -naphthol by coupling and oxidation. Its formula is

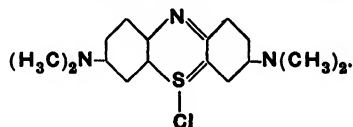


again the para-quinonoid group is present.

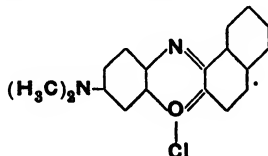
(b) *The Thiazines*, containing sulphur in the typical quinonoid group,



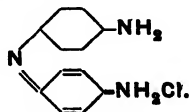
Methylene Blue is the most important member of this group; its formula is



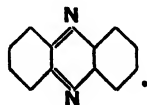
(c) *The Oxazines*. In these oxygen replaces the sulphur atom of the thiazines. Meldola's Blue is a typical example:



(d) *The Indamines* resemble the indophenols in structure, but have an  $=\text{NH}_2\text{Cl}$  instead of the  $=\text{O}$  grouping. Phenylene Blue is an example:

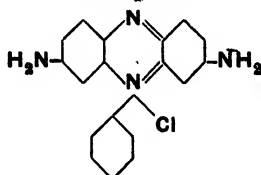


(e) *The Azines*, which are subdivided into (i) eurhodines, and (ii) aposafranines, safranines, and indulines. The azines are derivatives of (di)phenazine,

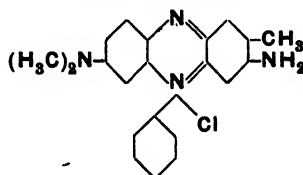


The amino derivatives of phenazine are termed *eurhodines*. In the *aposafranines*, *safranines*, and *indulines*, one of the nitrogen atoms of the phenazine molecule is combined with another benzene or naphthalene ring. The *aposafranines* are mono-amino or monohydroxy derivatives, the *safranines* diamino derivatives, and the *indulines* tri- or tetra-amino derivatives of the substituted phenazine. The following are examples:—

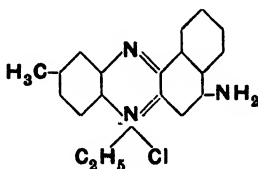
Safranin B.



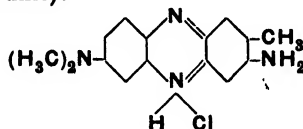
Rhoduline Violet.



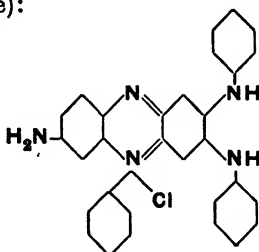
Induline Scarlet (aposafranin):



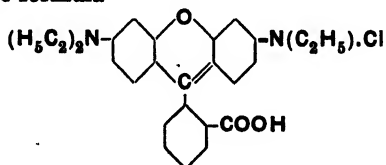
Toluylene Red (eurhodine):



Indamine Blue (induline):

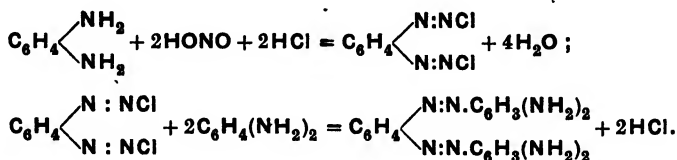


(3) *Rhodamines*.—These dyestuffs are related to the eosines. They contain carboxyl groups ( $-\text{COOH}$ ) together with amino or substituted amino groups. They have, therefore, the properties of both acid and basic dyestuffs. Rhodamine B has the formula

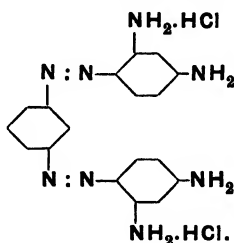


(4) *Gallocyanines*.—These are basic dyes which contain also the characteristic hydroxyl groups of the mordant class, and have the properties of both. As they are used generally as mordant dyestuffs, they will be dealt with later.

(5) *Azo Compounds*.—Bismarck Brown is an important example of an azo-basic dyestuff. It is made by treating three molecules of *m*-phenylenediamine,  $C_6H_4(NH_2)_2$ , dissolved in dilute hydrochloric acid with two molecules of nitrous acid, and precipitating the dyestuff by means of salt. This is an interesting example of diazotizing a base and then coupling it with itself. The reactions are—

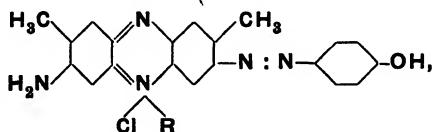


The dyestuff is the hydrochloride of the base and has the formula:



Bismarck Brown can be diazotized and developed on the fibre. When cotton dyed on a tannic-acid mordant is diazotized and developed with paranitraniline, a fast brown is obtained.

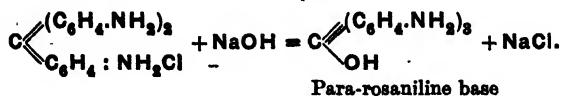
(6) *Basic Mordant Dyes*.—The Janus dyes contain both amino and hydroxyl groups, and are both basic and mordant dyestuffs; Janus Black has the formula:



where *R* is a radical such as  $-CH_3$  or  $-C_6H_4.CH_3$ . They dye both cotton and wool from an acid bath, and are used in dyeing unions. Silk can be dyed also from an acetic-acid bath. Wool can be dyed from an acid bath containing 2 to 4 per cent. of hydrochloric acid and 2 per cent. of chromium fluoride.

**Properties of Basic Dyes.**—The basic dyes are characterized by the brilliancy of the colours they produce on textile fibres, and their great tinctorial power. The latter property can be seen well by comparing the dyeing power of magenta and acid magenta. While about 5 per cent. of the latter is required to produce a full shade on wool, only from 2 to 3 per cent. of magenta is necessary. In some cases, full shades can be obtained with as little as 1 per cent. of the dyestuff. The basic dyestuffs are all readily soluble in alcohol or methylated spirit. They are not, as a rule, so readily soluble in water as the acid dyes, and unless care is taken when dissolving them they are liable to form a sticky mass, which is difficult to deal with. Some of them, like auramine, are decomposed by boiling water and are used at a temperature of  $140^\circ$  to  $150^\circ$  F. ( $60^\circ$ – $65.6^\circ$  C.). When a basic dye is treated with an alkali, it is decomposed

with liberation of the dye base. For example, with para-rosoaniline hydrochloride the reaction is:



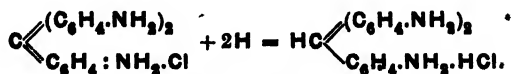
Many of the dye bases are only sparingly soluble in water. Thus, if sodium hydroxide is added to a solution of methylene blue, and the mixture allowed to stand for some time, a flocculent blue precipitate of the base will be seen to have formed. In all cases the base is less soluble if some salt be added with the sodium hydroxide. Water containing alkali or temporary hardness should never be used with basic dyestuffs without first neutralizing it with acetic acid. It should be remembered also that softened water generally contains sodium carbonate, calcium hydroxide, or unremoved calcium and magnesium bicarbonates. While many of the basic dyestuffs are decomposed only by strong alkalis such as potassium hydroxide, others give the dye base when treated with ammonia; and, again, some are hydrolysed by water alone. The liberated bases are all soluble in ether, and may be extracted by shaking with this solvent in a separating-funnel. These facts can be made use of in the separation of mixtures of basic dyestuffs.

When the base is extracted with ether, the solution is often of a different colour from that of the dyestuff, and sometimes has little distinctive colour; but if a little dilute acetic acid be added, the colour is immediately reproduced.

Basic and direct (or sulphur) dyestuffs combine directly with each other. They cannot, therefore, be used together in the same bath. But basic dyestuffs are used in *after-treating* cotton or other fabrics dyed with direct colours (see Chapter XXVII), the direct dyestuff acting as a mordant. Basic and acid dyestuffs combine also, and one may be used to estimate the other. Thus auramine can be estimated by titration with a standard solution of indigo carmine.

Another important property of the basic dyes is that, without exception, they combine with tannic acid to form an insoluble compound, provided mineral acid is absent. This precipitate is formed when a solution of tannic acid and sodium acetate is added to one containing the dyestuff. The sodium acetate neutralizes any hydrochloric acid liberated from the dyestuff, and so produces the conditions necessary for the precipitation of the tannic-acid compound. If a dyestuff does not give this precipitate, it cannot be a basic dye. This property has an important application in practical dyeing. The chief fault of the basic dyes is that they are fugitive to light and not particularly fast to washing. Their fastness can be increased by a process termed *after-treatment*. This consists in treating the dyed fabric with a solution of tannic acid in order to form the insoluble tannate. The shade is made somewhat dull by the process. It must be remembered that when one says that, as a class, basic dyes are fugitive, there are always exceptions. Methylene blue, for example, stands exposure to light quite well.

When treated with a reducing agent, many basic dyes absorb hydrogen, giving colourless or leuco compounds. With para-rosoaniline hydrochloride the reaction is



All of these leuco compounds, with the exception of those formed from azo dyes, are oxidized readily by oxidizing agents, sometimes by air, re-forming

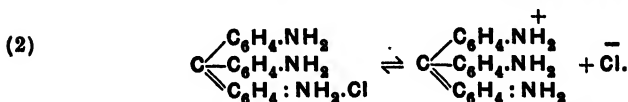
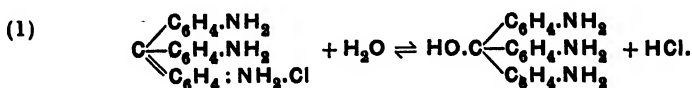
the original colouring-matter. Oxidation simply takes away the two atoms of hydrogen, introduced by reduction, in the form of water. Dyes which contain azo groups are split up into simpler nitrogenous compounds by reduction, and hence the colouring-matter cannot be reproduced by oxidation. The production of a leuco compound can be demonstrated by passing sulphur dioxide into a solution of magenta, when it gradually becomes colourless. If a little of the colourless solution is poured on to a filter-paper and exposed to air, the original colour is gradually reproduced.

Most of the acid dyestuffs are partly or completely stripped by boiling the dyed fabric with dilute ammonia or sodium carbonate solution, the ammonium or sodium sulphonate being re-formed, for which the fibre has no affinity. In a similar manner the basic dyes can often be removed from a fabric by boiling it with dilute acetic or hydrochloric acid. They can be removed also by treating the fabric with an alkali to liberate the dye base, and then extracting the latter with ether.

The basic dyes dye animal fibres directly, but do not dye cotton without the assistance of an acid mordant such as tannic acid. Bleached, and in particular over-bleached, cotton has, however, a considerably increased affinity for certain of the basic dyes, such as methylene blue, owing to the acidic nature of the fibres. Jute also has a considerable affinity for the basic dyes, but this is thought to be due to the presence of tannic acid in the fibre.

**Uses of Basic Dyestuffs.**—The basic dyes are used for dyeing knitting woollen yarns when particularly bright shades are required, which could not be obtained with an acid dye. Silk is very largely dyed with basic dyes. This fibre is used for fancy goods or dress materials where brightness of shade is of much greater importance than fastness to washing or even to light. A dyer never uses basic dyes on cotton if it can be avoided, since their use involves the troublesome process of mordanting with tannic acid. But, sometimes, bright shades are demanded, which can only be obtained with them. Rayons are often dyed with the basic dyes, nitro rayon having a direct affinity for them. They are used also for such purposes as making inks, typewriter ribbons, and dyeing leather.

**Theory of Dyeing with Basic Dyestuffs.**—The view is generally held that dyeing with these dyestuffs is chiefly a chemical process, depending either upon hydrolytic or electrolytic dissociation of the dyestuff in the bath, followed by chemical reaction with the wool fibre, resulting in the formation of a colour lake. These two forms of dissociation may, in the case of para-rosaniline, be represented by the equations:



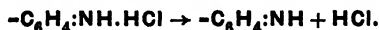
According to the chemical theory, the liberated base or basic ion combines with the carboxyl groups of the keratin or fibroin, hydrochloric acid remaining in the dye-bath or being adsorbed by the wool or silk.

It is an interesting fact observed by the authors (*J. Soc. Dyers Col.*, 1924, 40, 77) that de-amination increases the affinity for methylene blue. The quantities taken up in each case were estimated by titration. It is possible

that treatment with nitrous acid increases the number of carboxyl groups by converting amides into acids, thus:



Thorpe (*ibid.*, 1924, 40, 174) explained the dyeing of wool in the case of quinonoid dyestuffs by the fact that they readily form dissociated salts of the quinone-imine type, which are absorbed by the wool, leaving the acid in the bath, thus:



**Dissolving Basic Dyes.**—Owing to the relative insolubility of these colours, special precautions are necessary when dissolving them. The dyestuff is first made into a paste with about its own volume of 30 per cent. acetic acid or one-third of its volume of the strong acid. Sufficient boiling water is then poured on to the paste, with stirring, to dissolve the dye. In the case of auramine the temperature of the water should not be above 140° F. (60° C.). Stone or wood vessels should be used. Iron is unsuitable, since it is soluble in acetic acid. Clean copper is less objectionable. Weak methylated spirit may be substituted for acetic acid, since all the basic dyes are soluble in alcohol. The solution of the dye should always be strained through calico into the dye-bath, since, owing to the high tinctorial power of the basic dye, it is difficult to see undissolved particles.

**Assistants.**—The basic dyes have so great an affinity for both wool and silk, and also for mordanted cotton, that the presence of a retarding agent is often desirable. From 1 to 2 per cent. of acetic acid is generally used for this purpose. It acts by tending to inhibit the liberation of the dye base. When acid is used, the addition of a small quantity of alkali may be necessary towards the end of the dyeing to complete the exhaustion of the bath. Since the basic dyes will dye in a neutral bath, soap is also used as an assistant instead of acetic acid; from 10 to 15 per cent. is required. In this case only soft or softened water is permissible. With acetic acid, hard water may be used, since the acid neutralizes the temporary hardness. The quantity necessary for this should be determined and allowed for. With silk, boiled-off liquor or bast soap is the assistant commonly employed.

### Application of Basic Dyes to Silk.

**General Method.**—The bath is made up with 25 per cent. by volume of boiled-off liquor, just broken with acetic acid in the way described for acid dyes. The silk is wetted down in the bath at about 100° F. (37.8° C.). It is then lifted, and the dye solution is stirred in. The silk is then returned to the bath, and turned several times during the next twenty minutes. The temperature is then raised slowly to about 180° F. (82.2° C.), and kept at this value for about half an hour. With auramine and dyes decomposed by hot water, the temperature should not be allowed to rise above 140° F. (60° C.). Owing to the great affinity which silk has for the basic dyes, this method may give uneven results. Silk can be dyed also in a cold or lukewarm bath. The following method is often used: The dye solution is divided into three portions. One part is added to the cold or lukewarm bath, and the silk is worked carefully in this for about twenty minutes. It is then lifted, and the second portion of the dye is added. The temperature is now raised to about 100° F. (37.8° C.), and the silk put back and worked again for a further twenty minutes. It is lifted again, and the remaining dyestuff is added. The temperature is then raised to

140° F. (60° C.), the silk re-entered, and the dyeing completed by raising the temperature gradually to about 180° F. (82.2° C.). After dyeing, the silk is rinsed, hydro-extracted, and dried. If necessary it is scrooped in the usual way. The scrooping process is used also to brighten the colours and improve the lustre. Tartaric gives more permanent effects than acetic acid. Weighted silk is brightened also by working it in an olive-oil emulsion. About half a pound of olive oil is used for each 20 lb. of silk. It is emulsified by boiling it in water containing a little sodium carbonate.

Sometimes streaks or spots are visible on the dyed silk. These are due to one or both of the following causes: either the dyestuff has not been completely dissolved, and solid particles have become deposited on the goods; or the hardness of the water has not been properly neutralized, and the dye base has been precipitated on the fabric.

**Dyeing in a Neutral Soap Bath.**—For this process soft water is essential. If it is not obtainable, the water to be used must be boiled with a little sodium carbonate, allowed to settle, and the clear water drawn off. Ten to 15 per cent. of olive-oil soap is added to the bath. The silk is entered at 140° F. (60° C.), and worked in the bath till wetted out; it is then lifted, and a portion of the dyestuff is added. The temperature may then be raised to about 180° F. (82.2° C.), and the remainder of the dye may be added in portions, lifting the goods before each addition. When dyed, the silk must be thoroughly washed to free it from soap, and then brightened in the manner described above. The whole of the dyestuff may be added at the beginning, but this practice is not to be recommended, for it always incurs a risk of unlevel results. The neutral soap bath is used chiefly for yellow shades and Safranine and Diamond Magenta.

**Dyeing in a Bath acidified with Acetic Acid.**—This method is useful when boiled-off liquor is not obtainable, and can be applied with practically all the basic dyes. The acetic acid takes the place of bast soaps as a levelling agent, and imparts a softer feel to the silk. The bath should contain 8 oz. of acetic acid for every 100 gallons of water. The goods are entered cold, and the temperature is gradually raised to 180° F. (82.2° C.). The dyestuff should be added in portions during the dyeing operation, the silk being lifted before each addition of dyestuff. This method has the advantage that it makes subsequent brightening unnecessary.

**Dyeing Silk Skeins.**—Silk is usually dyed in skeins in the following way: The skeins are hung over smooth bent rods. These are laid across the top of the dye-bath, and continually moved from end to end of the bath. The skeins must also be turned at intervals; that is to say, the end resting on the rod must be raised vertically upwards so far as possible, and then allowed to drop into the bath in such a way that the end now resting on the rod is the one which was originally in the liquor. Two men, one on each side of the bath, are required to carry out this operation in a satisfactory manner. When large quantities of skeins are dyed, a machine can be used in which the poles carrying them are rotated by mechanical means.

**Dyeing Weighted Silk.**—Basic dyes are suitable for dyeing weighted silk. Beyond a thorough preliminary washing, no special precautions are necessary, and the methods described above are applicable.

**After-treatment of Basic Dyes.**—The fastness of basic dyes can be improved by treating the dyed goods with tannic acid, in order to form the tannate of the dye base. If this compound is then further treated with a salt of a metal which forms an insoluble tannate, a double compound of tannic acid with the metal and the dye is produced, which is still faster both to light and to washing.



For the latter purpose, antimony tartrate (tartar emetic) is used, since it forms a colourless and insoluble tannate. This salt is a double tartrate of antimony and potassium having the composition  $K(SbO)C_4H_4O_6$ . The treatment is carried out in the following manner: The dyed goods are worked in a bath containing about 1 per cent. of tannic acid. About twenty minutes at a temperature of 140° F. (60° C.) is sufficient, or they may be left for a longer time (say overnight) in a cold bath. They are then squeezed, transferred to a cold or lukewarm bath containing 0.5 per cent. of tartar emetic, and worked for about half an hour. They are then washed thoroughly to remove any uncombined antimony, and brightened in the usual way. In order to ensure that no soluble antimony is left which might cause skin irritation, the silk may be put back for a short time into the cold bath of tannic acid before being finally washed.

### Application of Basic Dyes to Wool.

Wool is dyed either in a neutral bath or in the presence of acetic acid. When a neutral bath is used, the addition of a readily soluble soap or Turkey-red oil aids penetration and acts as a levelling agent. The affinity of wool for basic dyes is very marked, and the dyeing should be started at a low temperature or even in the cold. Only soft water must be used in making up the bath. The following are the details of the two general methods:—

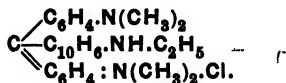
(1) **Dyeing in a Neutral Bath.**—The bath is made up with from 5 to 10 per cent. of olive-oil soap or Turkey-red oil. The goods, after wetting out, are entered at about 100° F. (37.8° C.), or sometimes at atmospheric temperature, a portion of the dyestuff having been previously added. After they have been worked for about fifteen minutes, the temperature is raised gradually to 140° F. (60° C.), when a second portion of the dye is added. After another fifteen minutes the remainder of the dye is introduced, and the temperature is raised to about 185° F. (85° C.), and dyeing is continued for half an hour at this temperature. The whole of the dye may be added to the bath at the beginning in the case of dyes which are known to be level dyers.

(2) **Dyeing with Acetic Acid.**—In this case no soap is used, but the bath is made up with from 1 to 2 per cent. of acetic acid, and since this tends to delay the dyeing, the whole of the dye may be added before entering the goods. Ten per cent. of Glauber's salt is sometimes used with acetic acid. Dyeing is started at about 100° F. (37.8° C.), and the temperature is raised slowly to 185° F. (85° C.) for about 30 to 45 min. If necessary, a little borax is added towards the end of the operation to neutralize the acid and liberate the dye base.

**Special Methods.**—*Victoria Blue*, which is used very extensively for wool, though a typical basic dye, is used in the same way as the acid dyes. The dye base is not soluble in water, nor even in weak acids. Hence, if the ordinary methods are employed, it is liable to be precipitated either in the dye-bath or on the goods. In the presence of the quantity of sulphuric acid used in the acid dye-bath the base is not precipitated. Hence the dye is used in exactly the same way as an acid dye, i.e. with 4 per cent. of sulphuric acid and 20 per cent. of Glauber's salt. The sulphuric acid may be replaced by 5 per cent. of acetic acid, or sodium bisulphate (10 to 15 per cent.) may be used.

*Victoria Blue* gives clear bright shades on wool, varying from sky blue to royal blue, all of which have considerable fastness. The shades are improved by a light stoving. This is the case with many other basic dyes. Instead of after-treatment by stoving, the goods may be dyed in the presence of sulphurous acid. For example, the bath is made up with 5 lb. of sodium bisulphite (70° Tw.) and 2 lb. of sulphuric acid for each 100 lb. of goods. Naturally,

allowance has to be made for loss of colour in stoving, and this makes it difficult to produce a given shade by the latter process. Victoria Blue is classified sometimes as an acid dye. That it is a typical basic dyestuff is seen from its formula (Victoria Blue R):



The *Rhodamines*, which are dyed from a bath containing a weak acid (2 to 3 per cent. of acetic acid), form a connecting link between the acid and basic classes.

*Methylene Blue* is used in a slightly alkaline bath containing from 1 to 2 per cent. of borax.

*Malachite Green* is dyed, sometimes, on what is termed a *sulphur mordant*. The mordanting bath is made up of 12 lb. of sodium thiosulphate (or "hyposulphite"), 6 lb. of alum, and 3 lb. of sulphuric acid of 168° Tw. for every hundred pounds of goods. The goods are entered at 100° F. (37·8° C.), and the temperature is then raised to 180° F. (82·2° C.). The goods are worked in the bath at this temperature for one hour, and then taken out and rinsed. There must be no metallic pipes in the mordanting bath, and the steam should be led in through a rubber pipe. The goods are then dyed in a neutral, or a faintly acid bath. *Methyl Green* also is applied in this way.

### Application of Basic Dyes to Cotton.

The method of application is somewhat complicated, involving mordanting with tannic acid before dyeing. Nevertheless, it is frequently made use of, since there are many bright shades required on cotton which are only obtainable with basic dyes on a tannic-acid bottom. Dyeing tannin-mordanted cotton with basic dyes is a rather difficult process, requiring a great amount of care, since the affinity of tannic acid for basic dyes is so great that unlevel shades are certain to be obtained unless every precaution is taken.

**Mordanting with Tannic Acid.**—Cotton does not combine chemically with tannic acid, but it has the power of adsorbing it from its solutions, particularly from a cooling bath. The general rule in mordanting is to use twice as much tannic acid as the quantity of dyestuff which is to be fixed on the fibre. This is weighed out and dissolved in water, and the cotton is wetted down and entered. The temperature of the bath is then raised to the boiling-point in order to expel air from the cotton and aid penetration. The goods are worked in the cooling bath for about two hours, and sometimes allowed to remain in it overnight. They are then removed and squeezed. Heavy goods are generally treated by passing them through a hot solution of the tannic acid and squeezing between rollers. The solution may be of about 3° Tw. strength. Since the tannic acid is only adsorbed, it would be removed by washing. Moreover, if it were put into the dye-bath, much of the tannic acid would be removed and form an insoluble compound in the dye-bath with the basic dye. To prevent this the tannic acid is next *fixed*, i.e. made into an insoluble compound by treatment with a metallic salt capable of producing an insoluble tannate. Antimony tannate is insoluble in water and also colourless. Hence for light colours the tannic acid is fixed by means of antimony. For dark shades or colours, iron is substituted, since it is much cheaper, but as iron tannate has itself a dark colour, this method cannot be used for bright colours or light shades. The conversion of the tannic acid into an insoluble tannate does

not affect its power of combining with basic dyes. In order to fix the tannic acid by means of antimony, tartar emetic (potassium antimonyl tartrate) is used. Half as much of this as the tannic acid used is required. It is dissolved in cold water, and the reaction of the solution tested with litmus-paper. If it is acid, the solution is carefully neutralized with sodium carbonate.

The goods, after coming out of the tannic-acid bath, are immediately put into the cold bath of tartar emetic, and worked about for thirty minutes. It is very important that the tannic acid should be fixed at once. If goods containing tannic acid are allowed to lie about exposed to air, light brown stains may be developed owing to absorption of oxygen. At the end of half an hour, the goods are taken out of the antimony bath and washed. They must then be dyed without delay. If this is impossible, they should be covered with a damp cloth to protect them from the action of air and light. But it is better not to mordant them till the whole process can be carried out. It is, of course, essential that there should be sufficient antimony in the fixing bath to combine with the whole of the tannic acid. It is better to have too much than too little. For this reason rather more tartar emetic than that given may be employed; or a standing bath is often used. In this case care must be taken to keep it just neutralized with sodium carbonate. When the tannic acid reacts with tartar emetic, potassium hydrogen tartrate is formed, and, if this is allowed to accumulate in the bath, it will prevent the formation of the insoluble tannate. Tannic acid also is used as a standing bath, being replenished each time it is used with about three-quarters of the original quantity. *Antimony salt*, which is a double salt of antimony fluoride and ammonium sulphate,  $\text{SbF}_2 \cdot (\text{NH}_4)_2\text{SO}_4$ , is used sometimes instead of tartar emetic, but its solution in water has a strongly acid reaction, and requires careful neutralization.

*Fixing Tannic Acid with Iron Salts.*—When bright shades are not required, copperas (ferrous sulphate) may be used as the fixing agent. For this purpose the tanned cotton is soaked for about half an hour in a cold bath containing from 3 to 5 per cent. of ferrous sulphate and 2 to 4 per cent. of ground chalk. The object of the latter is to neutralize the sulphuric acid which is formed.

**Tannic acid**,  $\text{C}_{14}\text{H}_{10}\text{O}_6 \cdot 2\text{H}_2\text{O}$ , is a common constituent of vegetable tissues. It is obtained from sumac leaves, gall nuts, myrobalans, chestnut wood, and other tissues. Commercial tannic acid and gall nuts are suitable for bright colours or light shades; sumac and myrobalans for dark colours. When a solution of tannic acid is exposed to air, it undergoes hydrolysis, with the formation of gallic acid,  $\text{C}_6\text{H}_3(\text{OH})_3 \cdot \text{COOH}$ :



At the same time atmospheric oxygen is absorbed, and dark-coloured compounds are formed. Tannic acid gives insoluble precipitates with solutions of gelatin, proteins, and many heavy metals.

**Dyeing the Mordanted Cotton.**—It has been mentioned already that the dyeing must be completed as soon as possible after the cotton is mordanted. The operation must be conducted with great care if a level colour is to be obtained, and, owing to the great affinity of tannic acid for the basic dyes, similar precautions are taken to those used in dyeing silk. The dyestuff is dissolved, and divided into three portions. The cotton is placed in a bath of cold water together with from 1 to 2 per cent. of acetic acid and one-third of the dye solution. It is worked in the cold bath for about fifteen minutes, or till most of the dye has been taken up. The second part of the dye solution is then added, and the temperature of the bath is raised slowly to about  $100^\circ \text{F}$ .

(37.8° C.). When the bath is again practically exhausted, the remaining dye is added, and the temperature is raised to about 160° F. (71.1° C.). After the dyeing has been completed, the goods are washed and dried.

**Back-tanning.**—The fastness of the colour is increased by a process termed *back-tanning*. After rinsing, the dyed goods are put, at once, into a cold bath containing about an ounce of tannic acid to each 10 gallons of water. After being worked in this bath for half an hour, they are squeezed, and transferred to a cold bath of tartar emetic of about half the strength of the tannic-acid bath. This is followed by thorough washing. Although back-tanning increases the fastness, it sometimes alters the shade.

**Single-bath processes** may be made use of for light shades. The goods are entered into a cold bath containing 3 to 6 per cent. of 50 per cent. acetic acid, 2 to 4 per cent. of tannic acid, and 0.25 to 1 per cent. of the dye. The temperature is raised slowly to 140° F. (60° C.), and dyeing is completed at this temperature. After this, the goods are squeezed, and worked for half an hour in a cold bath of tartar emetic. The process may, however, be reversed, the cotton being dyed at the boiling-point in a bath containing the dye, tartar emetic, and from 10 to 20 per cent. of common salt. After dyeing for three-quarters of an hour, the goods are lifted, the tannic acid is added to the bath, and the goods are re-entered and allowed to stand for from half an hour to an hour in the cooling bath.

**Difficulties in Dyeing Mordanted Cotton.**—If the mordant is not evenly distributed, it is impossible to get level dyeings. The dyestuff can be fixed only where the mordant is. Streaky or patchy mordanting must give the same effect when the goods are dyed. Apart from uneven adsorption of the tannic acid, trouble may be caused by (i) letting the goods lie about between the processes, so that the exposed parts become dry or partly dry; (ii) allowing iron to come into contact with the tanned goods, or using ferruginous water; and (iii) differences in the cottons used in making the original yarn.

**Mordanting with Katanol.**—Katanol is a synthetic product made by heating phenols with sulphur and a little iodine, the latter acting as a catalyst. It has a direct affinity for cotton, and forms insoluble compounds with basic dyestuffs. Its use in dyeing cotton with basic dyestuffs simplifies the process considerably, since no fixing of the mordant is necessary. From 2 to 3 per cent. of the substance is dissolved in a hot 2 per cent. solution of sodium carbonate; the cotton is treated with the solution for two hours at 140° F. (60° C.), then rinsed with water, and dyed in a "long" liquor at 105° F. (40.6° C.), the dyestuff being added in portions. *Tamal*, which is a formaldehyde compound of naphthalene-sulphonic acid, acts in the same way as katanol.

**Mordanting with Fatty Acids.**—These, owing to their acid nature, are mordants for basic dyes, but do not give such fast colours as tannic acid. The cotton is worked in a lukewarm bath containing 7 to 8½ lb. of Marseilles soap and 175 gallons of water for every 100 lb. of cotton. The hardness in the water should first be removed with sodium carbonate. The cotton is then wrung out, and transferred to a cold bath containing 3 oz. of chloride of tin for every 10 gallons of water. After working in this bath for half an hour, the goods are transferred to a lukewarm bath containing 2 to 3 lb. of dyestuff, 1 to 2 lb. of alum, and 176 gallons of water for every 100 lb. of cotton. This bath is allowed to cool down while the goods are worked in it for half an hour. When dyed, the goods are not rinsed, but merely squeezed out and hydro-extracted. Better results are obtained by using Turkey-red oil and sulphonated soap. The cotton is worked in 1-lb. lots, one lot being taken in each hand, in a liquor composed of 1 part of oil to 2 parts of water. After each lot has

been mordanted, another pint of the above liquor is added to the bath. The yarn; after its first immersion, is completely dried at a moderate temperature, and then mordanted again in the same liquor, and sometimes it is mordanted even three times. The mordanted yarn is dyed in a cold bath containing 150 gallons of water for every 100 lb. of goods. The dyestuff is added in portions, and the bath may be acidified with acetic acid. The method described above is simpler and gives better results than the old method in which Turkey-red oil and aluminium acetate were used. In this process the yarn is worked in handfuls in a liquor of 1 part oil to 9 of water and, after drying, worked in a bath of aluminium acetate of  $7\frac{1}{2}^{\circ}$  Tw. The goods are then treated at  $115^{\circ}$  F. ( $46.1^{\circ}$  C.) for half an hour in a bath which contains 150 gallons of water and  $17\frac{1}{2}$  lb. of chalk for every 100 lb. of cotton. This whole cycle is repeated once more, and then a third time, but the treatment with chalk is now omitted, the goods being rinsed lightly, and dyed without drying, when they come out of the aluminium-acetate bath. This method gives a harsher feel to the cotton than when Turkey-red oil alone is used as the mordant. Though basic dyes on a fatty-acid mordant run badly in water, yet the process has the advantage of giving brighter shades than when tannic acid is used.

**Mordanting with Direct Dyes.**—This method is chiefly used for *topping* colours dyed with the direct dyestuffs. It will be described in Chapter XXVII. Sometimes a direct colour which is very close to the required shade is added to the tannic-acid bath in mordanting the cotton. This gives a grounding on the cotton, which can afterwards be brought up to the desired shade with the basic dye.

**Basic Dyes which have a Direct Affinity for Cotton.**—A limited number of basic dyes have a direct affinity for cotton, particularly in the "grey" or unbleached state. The colours obtained are, however, by no means fast. The following dyestuffs made by I.C.I., Ltd., belong to this class: Auramine O, Rhodyl 4G, magenta crystals, magenta powder P and 2B, Methyl Violet 2B and 10BL, Marine Blue 81,554, Methylene Blue GS and T50, New Methylene Blue S, and Turquoise Blue G.

Auramine and Rhodyl 4G are also suitable for bleached cotton. From 0.5 to about 2.5 per cent. of the dyestuff is used, according to the shade required. No assistant is employed, and the only precaution to be taken is that the temperature should not be raised above  $110^{\circ}$  F. ( $43.3^{\circ}$  C.) when dyeing with Auramine, otherwise the dyestuff will be decomposed. Bismarck Brown and Chrysoidine also have a direct affinity for cotton, but the colour is not fast. Much faster colours, however, may be obtained by padding the cotton with these two dyes, and then coupling them with diazotized para-nitro-aniline (see Chapter XXVIII).

## CHAPTER XXVII.

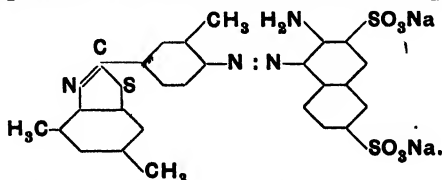
### THE SUBSTANTIVE OR DIRECT DYESTUFFS.

THE substantive dyestuffs, known also as *direct dyestuffs* or *salt dyestuffs*, or simply *cotton colours*, differ from those already described in that they dye cotton and other vegetable fibres directly, without the intervention of a mordant. For this reason they are always used for cotton when possible. They also dye both wool and silk directly, and are used to a certain extent for these fibres; and largely for dyeing mixtures of wool and cotton when both fibres have to be dyed the same colour.

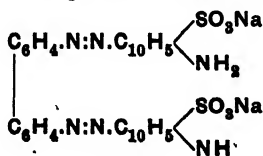
The discovery of Congo Red by Böttiger in 1884 has been referred to in Chapter I. This discovery, which was followed quickly by the preparation of many other similar colours, marked the opening of a new era in cotton-dyeing. Before 1884 cotton could be dyed only on a mordant or by means of indigo. Both of these processes are troublesome and expensive. But in cotton-dyeing cheapness of production and simplicity of method are of the greatest importance, and hence the substantive dyes gave an enormous impulse to the cotton-dyeing industry. The colours are not to be compared in fastness with those produced by mordant dyes or indigo, but cotton-dyeing is essentially a "cheap" trade, and fastness is often of only secondary importance.

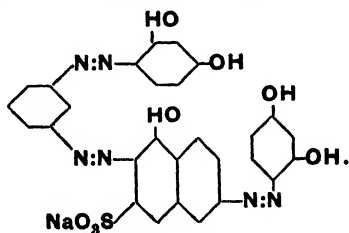
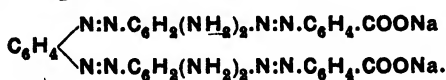
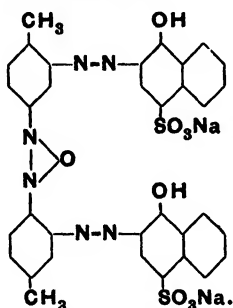
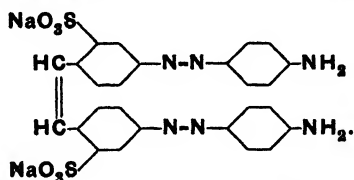
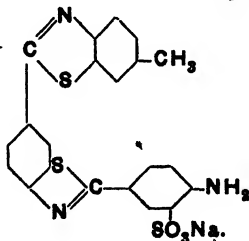
**Chemical Nature.**—The direct dyestuffs are, with a few exceptions, sodium salts of complex sulphononic acids. The common chromophore is the azo group, one to four of which may be present in each molecule. Since they are sodium sulphonates, they will dye wool from an acid bath, but all of them will dye it also from a neutral bath, as well as cotton and silk. When an acid dyestuff dyes wool, it is the sulphononic acid which combines with the fibre. In the case of a direct dyestuff, unless mineral acid is present, the dye molecule is taken up as a whole. The direct dyestuffs have as a rule higher molecular weights than the acid dyestuffs, their aqueous solutions have marked colloidal properties, and in some respects they resemble the neutral-dyeing acid dyestuffs; in fact, the two classes have no sharp line of demarcation. The following are examples of direct dyestuffs:—

- (1) *Monazo Compounds.*—Salmon Red, a thiazole compound,



- (2) *Disazo Compounds.*—Congo Red (benzidine derivative),



(3) *Trisazo Compounds*.—Diamine Fast Bordeaux,(4) *Tetrakisazo Compounds*.—Direct Brown S,(5) *Azoxy Dyestuffs*.—Rosophenine 4B,(6) *Derivatives of Stilbene*,  $\text{C}_6\text{H}_5.\text{CH}:\text{CH}.\text{C}_6\text{H}_5$ .—Cotton Brown R,(7) *Thiazole Dyes*.—These contain the  $-\text{C} \begin{smallmatrix} \text{N-} \\ \text{S-} \end{smallmatrix}$  group; e.g. Primuline,

**Properties.**—These dyes are, as a rule, readily soluble in water. A few which are somewhat sparingly soluble are dissolved in dilute sodium carbonate solution, while the azoxy dyes require sodium hydroxide. Although soluble in water, the substantive dyes do not in all cases give clear solutions. With

some the solutions become clear when heated, and again opalescent or cloudy when cold. This is due to the fact that they tend to give colloidal rather than true solutions with water. Their solutions dye all kinds of fibres directly, but some of them, such as Anthracene Red, contain hydroxyl groups, and have also the properties of mordant dyes. Although the direct dyestuffs dye cotton very readily, the colours obtained are by no means fast. In particular they generally *bleed*. If a piece of cotton dyed with a direct dye is boiled with soap and water which contains also a small piece of undyed cotton, the latter generally becomes stained with the dye from the former. This is known as *bleeding*. In some cases the colouring-matter can be largely removed by boiling with water alone. This lack of fastness and tendency to bleed is overcome, to a certain extent, by various processes of *after-treatment*. In fact, after-treatment is a very important part of dyeing with the direct dyestuffs. Soluble direct dyes are less soluble in solutions of salt, and can be salted out with excess of this body. In some cases (*e.g.* Congo red and benzopurpurines) the colours are very sensitive to acids. Congo red is used, on this account, as an indicator in chemical laboratories. All direct dyestuffs combine with basic dyes to give compounds which are less soluble than the original direct dye. Hence these dyes cannot be used in the same baths, though the reaction forms the basis of one method of after-treatment, known as *topping*. Many direct dyes are precipitated from their solutions by compounds of calcium and magnesium, and for this reason only soft or softened water should be used when dyeing. All direct dyes containing amino groups can be diazotized on the fibre, and afterwards coupled with suitable organic compounds.

Direct dyestuffs dye all fibres from an aqueous solution containing salt or Glauber's salt. Cotton can be dyed also in the presence of a little mild alkali; and wool with a little acid. On the other hand, cotton is not dyed in the presence of acid; and alkalis prevent the dyeing of wool and silk. When wool is dyed in an acid bath, the dyeing action is that of the liberated sulphonic acid, as in the case of acid dyestuffs.

**Theory of Dyeing with Direct Dyes.**—The dyeing of cotton with direct dyes is a fact which is very difficult to explain by the chemical theory. The physical explanations therefore find most favour in this case. Witt (*J. Soc. Chem. Ind.*, 1891, 10, 42) and Cross and Bevan (*ibid.*, 1894, 13, 354) believed that the substantive dyeing of cotton is due to the formation of a solid solution of dyestuff in the fibre. The dyestuff is more soluble in cellulose than in water, and is consequently extracted from its aqueous solution. The function of the assistants used (*i.e.* common salt and Glauber's salt) is to render the dye less soluble in water, and therefore relatively more soluble in the fibre.

Weber (*J. Soc. Chem. Ind.*, 1894, 13, 120) expressed the opinion that direct dyes attach themselves to cotton as whole molecules. Gnehm and Roteli (*ibid.*, 1898, 17, 660) confirmed this view by dyeing cotton with the barium salts of certain direct dyes which are also sulphonic acids. The amount of barium left in the fibre after dyeing was estimated, and the results showed clearly that the salts were adsorbed as whole molecules. This is strong evidence in favour of the view that substantive dyeing is a physical phenomenon. Gnehm and Kaufer (*ibid.*, 1902, 21, 611) proved that the free acids of the direct dyes would also dye cotton. The fibre was dyed with both the free acid and the sodium salt of benzopurpurine. The cotton dyed with the salt was then washed with strong hydrochloric acid, when it became blue. When all the sodium had been washed out, however, the original colour was permanently restored. -



Bilz (*J. Soc. Chem. Ind.*, 1903, 22, 1126) showed that colloidal solutions of selenium and gold behaved towards textile fibres in a manner very similar to the substantive dyes, and from this he concluded that dyeing with these colours could be explained by adsorption. Both elevation of the temperature and addition of salt to the bath cause colloidal solutions of these elements to dye the fibre more deeply. The presence of a protective colloid in the bath, on the other hand, causes dyeing to be slower, with the result that a more level shade is obtained. Hübner (*ibid.*, 1907, 26, 866) studied the behaviour of various inorganic substances, such as graphite and charcoal, towards dyestuffs. Charcoal and graphite were treated with Benzopurpurine 4B, and then topped with Night Blue. The results of the experiments led him to conclude that dyeing with direct dyes, as well as with those of other classes, was a purely mechanical process.

There is, therefore, a considerable amount of evidence in favour of the physical explanations of the substantive dyeing of cotton. Attention has already been drawn, however, to the fact that acetylation of the hydroxyl groups causes cotton to lose its affinity for the direct dyes (p. 136).

That the hydroxyl groups of the cellulose molecule are in some way concerned in the dyeing of cotton with direct dyestuffs is indicated by the fact that if they are replaced by acetyl groups, the resulting cellulose acetate loses its affinity entirely, but regains it when saponified. Briggs (*J. Soc. Dyers Col.*, 1924, 40, 190) concluded as the result of experiments that in neutral or alkaline baths, direct dyes are electro-negative colloids, capable of a high degree of dispersion in the absence of destabilizing agents. The dyeing with these dyes is merely a case of adsorbing a colloid from suspension. Weak flocculating agents increase the amount of dye taken up by the fibre, provided that the dye is not thrown out of suspension during the process of dyeing, in which case a flocculating agent sufficiently active to produce coagulation will decrease the amount of dye adsorbed. Peptising agents decrease the adsorption of the dye, unless the agent is a second colloid, itself strongly adsorbed, in which case it may carry dye with it on to the fibre and thus increase adsorption.

This theory suggests that a decrease in adsorption may occur when sufficient quantities of salt are added to cause actual flocculation. This was the case with Erie Red 4B and sodium chloride; the dye adsorbed was—

1/8 mol NaCl per litre.	32.5 mg.
1/4 " " " "	36.5 "
1/2 " " " "	33.0 "
2/1 " " " "	28.0 "

There was evident turbidity of the bath at the point of maximum adsorption and visible flocculation at the twice-molar concentration.

The action of direct dyes on animal fibres also must be explained by physical rather than chemical causes, but when an acid bath is employed it is probably the liberated sulphonic acid which is the active dyeing agent, and here the chemical theory offers a suitable explanation, as it does in the case of the acid dyestuffs.

**Assistants.**—Dye-baths made with direct dyestuffs are very difficult to exhaust, probably owing to the marked solubility of the dyestuff in water. Standing baths are quite commonly used for this reason. But the addition of sodium chloride or sulphate to the bath lowers the solubility of the dyestuff, thus assisting exhaustion, and these are the "assistants" commonly employed. There is, in the case of these dyestuffs, no necessity for the presence of an assistant to promote level dyeing. Owing to their great solubility and bad

exhausting properties, there is no difficulty in getting level colours. The assistant is, in fact, used rather for the opposite purpose, namely, to accelerate the rate of deposition of the dyestuff and not to retard it, as with the acid dyestuffs, for when the bath shows a disinclination to exhaust, more salt is added. With the same quantity of dyestuff and water the depth of the shade produced is partly determined by the quantity of salt present. This can be seen by dyeing several 10-g. lots of cotton side by side with the same quantities of dyestuff and water, but with increasing amounts of salt from none up to, say, 40 per cent., when a series of gradually increasing shades will be obtained. Glauber's salt acts in the same way, and is commonly used for light shades, sodium chloride replacing it for heavy shades. When from 0.1 to 0.5 per cent. of the dyestuff is used, from 10 to 15 per cent. of Glauber's salt is added to the bath. For from 0.5 to 4 or 5 per cent. of the dyestuff, from 10 to 40 per cent. of sodium chloride is used; but as much as 100 per cent. may be employed when heavy shades are required. If the solid-solution theory of the action of these dyes is accepted, it is obvious that the function of the salt must be to render the dyestuff less soluble in water, and consequently more soluble in the fibre. From the point of view of the colloidal theory, the function of the salt would be to increase the size of the colloidal aggregates of the dyestuff, and thus to make easier their coagulation on the fibre.

Besides salt, sodium carbonate is sometimes used as an assistant in the case of the less soluble dyes, and since only neutral or slightly alkaline baths are used, Turkey-red oil may be added to assist the dye liquors to penetrate heavy goods. The effect of sodium chloride upon the shade produced may be termed the *salt factor*. There are other factors which must be considered also, namely, (i) the temperature factor, and (ii) the concentration factor.

**Effect of Temperature.**—As a general rule, the effect of increasing temperature is to increase the affinity of a fibre for a dyestuff. Thus, it has been noted that the affinity of the acid dyes for wool increases gradually as the temperature rises to the boiling-point. Similarly, with silk it increases, as a rule, up to a temperature of about 180° F. (82.2° C.); but above this point it decreases again, and at the boiling-point some of the acid dyes have practically no affinity for silk. This may be called the *temperature factor*. In the case of the substantive dyestuffs it plays a rather important part. The dyestuffs of this class do not all act in the same way. While, in general, their maximum affinity for cotton is developed at the boiling-point, there are very many exceptions. Thus, Chrysophenine dyes cotton a full shade at 100° F. (37.8° C.), but Benzo Fast Scarlet 4B has practically no affinity for cotton at temperatures below 140° F. (60° C.). Again, a great many of the direct dyes will dye cotton in a cold or lukewarm bath in the presence of Glauber's salt or sodium chloride, though a full shade is not produced till the temperature of maximum affinity is reached.

Wool differs from cotton in that it has practically no affinity for most of the direct dyes in cold or lukewarm baths, but develops a strong affinity at higher temperatures, rising as a rule to a maximum at the boiling-point.

As a rule, the affinity of wool for direct dyes at the boiling-point is greater than that of cotton, while at lower temperatures the opposite obtains. Thus, in dyeing unions of cotton and wool, different shades may be obtained on the two fibres at different temperatures. As a general rule, the wool tends to become more deeply dyed at the boiling-point, and at lower temperatures the cotton. These facts may be made use of in dyeing unions to a solid colour. If, after boiling the goods with the dyestuff, the wool is more deeply dyed than the cotton, a little more dyestuff may be added and the bath allowed to

cool off, thus allowing the cotton to take up the dye more readily than the wool. If, on the other hand, the wool is less deeply dyed than the cotton, more dye may be added and the boiling continued till the colour of the wool is the same as that of the cotton.

Whilst many direct dyestuffs do not dye different fibres equally, some, on the other hand, will dye two or more to a solid shade. Information on this point is given in manufacturers' catalogues.

**Concentration Factor.**—When there is a strong affinity between a fibre and a dyestuff, the volume of the dye-bath may vary considerably without affecting the resulting colour of the dyed material. But in the case of the substantive dyes, where, owing to lack of affinity, it is difficult to exhaust the dye-bath, the volume of water used, *i.e.* the concentration of the dye solution, must be taken into account. When a dye-bath contains only relatively little water compared with the weight of the goods, it is termed a *short* bath, one containing a large proportion of water being *long*. With direct dyes, other conditions being the same, the shade produced increases with the shortness of the dye-bath, since this has the effect of making the dyestuff relatively more soluble in the fibre. Hence, with these dyes, when full shades are required, as short a bath as is compatible with free working of the goods should be used. When making a dyeing formula to give a certain shade, the concentration of the bath should always be taken into account and stated. If this is omitted, the formula will produce different shades according to the volume of water used in making up the dye-bath. It should be remembered also that when a dye-bath is heated by means of live steam there is progressive dilution, particularly if the dyeing is started cold.

For particulars of the rate of dyeing with direct cotton dyes, and method of estimating the rate of migration, see p. 527.

**Standing Baths.**—The low power of exhaustion of the substantive dyestuffs entails a considerable amount of waste if fresh liquors have to be used frequently. It is more economical to keep standing baths, whenever possible, especially for heavy shades, where a large percentage of the dyestuff has to be used. But, to obtain constant results, the concentration of the bath with respect to sodium chloride and dyestuff must be kept fairly constant. Standing baths are largely used for blacks and other dark shades. The usual practice is to add three-quarters of the original percentage of dyestuff with each fresh lot of goods. The sodium chloride factor is controlled by taking the density of the liquor at 60° F. (15.6° C.) with a hydrometer, and adding just enough sodium chloride to bring it up to about 2° Tw. for light, and to from 6° to 8° Tw. for heavy, shades.

### Application of the Direct Dyestuffs to Cotton.

**General Method.**—The dye-bath is usually made up with twenty times as much water as cotton, *i.e.* 2000 lb., or 200 gallons, of water for each 100 lb. of cotton. Soft water should be used, since some of the direct dyes are precipitated by salts of calcium and magnesium.

From 0.5 to 5 per cent. of the dyestuff is added (previously dissolved in water), according to the shade required. In the case of blacks even more may be necessary. Chlorazol Black SB, for example, requires 8 per cent. for a full shade. The dyestuff is dissolved in the usual way, by making it into a paste with cold water and then adding sufficient hot water to dissolve it. Distilled or condensed water should be used, or, at any rate, softened water. It is advisable to take the precaution of straining the solution into the dye-bath.

From 10 to 40 per cent. of crystalline Glauber's salt, or from 5 to 30 per cent. of sodium chloride, is next dissolved in the bath. The cotton is wetted out in hot water, or hot water containing a little sodium carbonate, and entered into the bath at about 140° F. (60° C.). The temperature of the bath is then raised gradually to the boiling-point, and dyeing is continued at this temperature for about an hour. If the shade is correct, the goods are then washed, hydro-extracted, and dried. If the depth of the shade is not quite sufficient, a little more dyestuff is added, and the dyeing continued for a short time either at the boiling-point or, in the case of cotton, in a cooling bath. With heavy goods, or when they are difficult to penetrate, Turkey-red oil may be added to the bath as an assistant. About half a pound for 100 gallons is sufficient.

**Cold Bath for Cotton.**—Practically all the direct dyes will dye cotton in a cold bath, and on some occasions such a bath is useful, as, for instance, when the goods contain wool, which it is desired to leave undyed. The bath is made up with the dyestuff and sodium chloride in the usual way, but soap or Turkey-red oil should be added to assist penetration.

**Soda-ash Bath.**—Some direct dyestuffs give better results if used in a slightly alkaline bath. In fact it is advantageous in most cases, since it renders the dyestuff more completely soluble in the dye-bath. From 0.5 to 2 per cent. of sodium carbonate may be used, but other mild alkalis, such as borax or sodium phosphate, are also suitable. The sodium carbonate aids penetration, and since it increases the solubility of the dyestuff, makes the dyeing rather slower. The operation is carried out in the usual way, except that the sodium chloride is sometimes added in portions. Alkali must not be used with certain dyestuffs, such as Chlorazol Yellow GX and Chlorazol Green BN; and with Dianol Fast Yellow 5GK, 2 per cent. of sodium phosphate, 2 per cent. of soap, and 20 per cent. of Glauber's salt are recommended.

According to Whittaker, the use of sodium carbonate has the disadvantage of increasing the liability of the colour to run. Goods dyed in this way should not be left lying about, but should be thoroughly hydro-extracted and dried at once, as evenly as possible.

**After-treatment.**—The direct dyes, as mentioned above, suffer from lack of fastness. Although, of course, the degree of fastness varies considerably, yet with comparatively few exceptions they bleed badly. Their fastness to light, washing, acids, etc. also varies very much, but is, on the whole, poor. These defects can, however, be remedied to a considerable extent by after-treatment of the dyed goods. There are many processes, which include (i) after-treatment with metallic salts; (ii) topping with basic dyes; (iii) after-treatment with formaldehyde; (iv) after-treatment with sodium carbonate; (v) after-treatment with bleaching powder; (vi) brightening with soap and oil; (vii) changing the dyestuff into another on the fibre by (a) diazotizing and developing it, or (b) coupling it with a diazotized base.

These processes are not applicable indiscriminately. Some are suitable for particular dyestuffs, and others not. The particular processes to be used are, to a certain extent, dependent upon the constitution of the dyestuff, and considerable experience is necessary in their application.

*After-treatment with Metallic Salts.* This includes the use of—

(a) *Copper sulphate.* The dyed cotton is worked at 140° F. (60° C.) for from 15 to 30 min. in a bath containing from 0.5 to 2 per cent. of crystalline copper sulphate. This process is used chiefly to increase fastness to light. It is suitable for blues and browns and certain yellows and reds, among which are the following chlorazol dyestuffs: Fast Yellow 5 GK, Fast Red F, Brown M, Sky-blue FF, and Blue RW. Other dyestuffs improved by this treatment are

Azo Blue, Direct Red J, Congo Cyanine B, Diamine Blue, Heliotrope B, Congo Blue 2PB, and Diamine Brilliant Blue G.

(b) *Chromium fluoride*. The dyed goods are boiled for 30 min. in a bath containing from 1 to 4 per cent. of chromium fluoride. This process improves fastness to washing in the case of a number of dyestuffs, including Chlorazol Fast Red F, Chlorazol Green G, Cotton Orange G, Azo Black-blue B, and Tri-sulphone Blue B.

(c) *Potassium dichromate*. The dyed cotton is worked at 160° to 195° F. (71.1°–90.6° C.) in a bath containing from 0.5 to 2 per cent. of potassium dichromate and the same quantity of acetic acid. This process also gives increased fastness to washing with the same kinds of dyes as the chromium fluoride process, to which it is generally preferred.

(d) *Copper sulphate and potassium dichromate*. It has been explained that copper salts improve the fastness to light, and chromium salts improve that to washing. There are a number of direct dyes which may be simultaneously treated with both chrome and copper sulphate, in this way improving fastness to both light and washing at the same time. The dyed cotton is worked for 15 to 30 min. in a bath at 140° F. (60° C.) containing 0.5 to 2 per cent. of copper sulphate, 0.5 to 2 per cent. of potassium dichromate, and 0.5 to 2 per cent. of acetic acid (30 per cent.). The following are a few dyes which are commonly after-treated in this way: Chlorazol Brown M, Diphenyl Brown BM, Direct Blue R, Chlorazol Sky-blue FF, and Dianil Yellows.

**Topping with Basic Dyes.**—When a solution of a basic dye is added to a solution of a direct colour, the two dyes precipitate each other with the formation of an insoluble colour lake. It is owing to this property that direct dyes act as mordants to basic colours. The process of after-treatment with basic colours of cotton dyed with substantive dyes is known as *topping*, and it gives both a faster and a brighter shade, though it is for brightness rather than fastness that the process is used. It is very often useful when the cotton cannot be brought up to the exact degree of brightness to match a sample with direct colours alone. The shade may or may not be altered by topping, according to whether the basic dye is of a different or of the same colour to the bottom already on the fabric. The dyed cotton is usually topped by working it for about 15 min. in a cold bath which contains from 0.25 to 0.5 per cent. of the basic dye. Two per cent. of acetic acid may be added as a retarding agent if necessary, and in some cases it is advisable to add the basic dye in portions. A much faster colour can be obtained by adding 2 to 4 per cent. of tannic acid to the substantive bath, squeezing the dyed cotton, working it for 20 min. in a bath containing 1 to 2 per cent. of tartar emetic, and finally topping with the basic dye.

*After-treatment with Formaldehyde.*—The fastness to washing of many direct colours is considerably improved by after-treatment with formaldehyde. The Vulcan colours of Messrs. I.C.I., Ltd., when treated in this way, acquire excellent fastness to both washing and cross-dyeing, while their fastness to light is improved by treatment with copper salts. The dyed cotton is worked for 15 min. in a bath containing 0.5 to 2 per cent. of 40 per cent. formaldehyde and 1 to 2 per cent. of 30 per cent. acetic acid. The temperature of the liquor should be about 180° F. (82.2° C.) or nearly at the boiling-point. A cold or warm bath may be used also, the treatment being prolonged to half an hour.

*After-treatment with Sodium Carbonate.*—This is chiefly used with colours such as Congo red, which are sensitive to acids. The dyed cotton is worked for 30 min. in a boiling bath which contains 5 per cent. of sodium carbonate.

*After-treatment with Bleaching Powder.*—This process is used only with Primuline. This gives a beautiful yellow colour, which, however, suffers greatly from want of fastness. But if it is treated with a cold solution of bleaching powder of 1° Tw. strength for about 15 min., the yellow is changed to a brownish yellow, which is much faster to both light and washing.

*Brightening with Soap and Olive Oil.*—This treatment is commonly applied to blacks of all kinds, not to improve their fastness, but to increase the brightness and to give a fuller black. The dyed goods are worked for about 20 min. in a lukewarm emulsion of olive oil in a soap solution, and then hydro-extracted and dried without washing. A soap solution containing about 5 g. of olive-oil soap and 1 g. per litre of olive oil may be used.

*Brightening with Tannic Acid and an Iron Salt.*—Direct blacks on cotton are improved also by after-treatment with tannic acid and an iron salt, or by topping with aniline black or logwood. In the former method the dyed cotton is steeped in a bath containing 10 per cent. of sumac extract at a temperature of 140° F. (60° C.). It is then squeezed, and transferred to another bath containing a cold solution of ferrous acetate of about 3° Tw. density. After this it is washed and dried. Topping with aniline black or logwood will be described later.

*After-treatment by diazotizing and developing or by coupling* is described fully in the next chapter.

### Application of the Direct Dyes to Wool.

The direct dyestuffs are quite suitable for wool, giving, as a rule, faster shades than on cotton. They may be used in a neutral bath in the same way as for cotton. But wool has practically no affinity for these colours at temperatures below 140° F. (60° C.); this becomes marked only at 180° F. (82.2° C.). Thus cotton may be dyed in a lukewarm bath with a selected direct dye, leaving the wool practically colourless. This effect is more marked if soap, Turkey-red oil, or sodium carbonate is added to the bath. These tend to keep the colour off the wool, but do not affect the affinity of the cotton. If, on the other hand, the dyeing is conducted at the boiling-point, in many cases the wool is more deeply dyed than the cotton; in others the reverse may obtain; while, again, many direct dyes dye both fibres alike. But in most cases, if the boiling bath is made faintly acid, the wool will take up nearly all of the dye, leaving the cotton often nearly white. This is because the direct dyestuffs contain sulphonie-acid groups, and the free sulphonie acid is liberated when the bath is acidified. These act in a similar manner to the dye acids of the acid dyestuffs. This can be made use of in the application of the direct dyestuffs to wool, and to assist the exhaustion of the dye-bath. But only a weak acid can be used. If a strong acid, such as sulphuric, is employed, the affinity of the wool for the liberated sulphonie acids is so great that uneven dyeing results. In a similar manner, the presence of alkali in the dye-bath tends to keep the dyestuff off wool and to cause it to accumulate on cotton.

In dyeing by this method, the goods are entered into the bath at about 140° F. (60° C.). The bath contains, in addition to the dyestuff, from 1 to 2 per cent. of acetic acid and from 10 to 20 per cent. of Glauber salt. The temperature is raised gradually to the boiling-point, and dyeing is continued in the gently boiling bath for about three-quarters of an hour. If the exhaustion of the bath is not good, it can be assisted by the addition of a little more acetic acid. It is better, in many cases, to use 5 per cent. of ammonium acetate instead of acetic acid, since this ensures the gradual liberation of acetic

acid in the boiling bath. About 1 per cent. of acetic acid added towards the end of the operation will assist exhaustion. Dyestuffs like Congo red and Benzopurpurine, which are affected by acids, cannot, of course, be used in this way, but must always be dyed from a neutral or even faintly alkaline bath.

The direct colours may be after-treated on wool in the same way as for cotton. When using metallic salts, if the exhaustion of the bath is good, these may be added directly, together with about 3 per cent. of acetic acid. If exhaustion is incomplete, the treatment must be carried out in a separate bath.

#### **Application of the Direct Dyes to Silk.**

Silk resembles wool in that it has a considerable affinity for substantive colours in a neutral, but a still greater affinity in an acid, bath. The shades obtained with these dyes on silk are of relatively good fastness, but are wanting in brilliancy of shade. This may, however, be overcome by topping with a small amount of a basic dye. Silk is dyed from a faintly acid, boiled-off liquor or soap bath. The goods are entered at 140° F. (60° C.), and the temperature is then gradually raised to the boiling-point. Or, as an alternative, one may use a bath containing 5 to 10 per cent. of Glauber's salt and 4 to 5 per cent. of acetic acid. It is important, however, that the acid should be added in portions during the dyeing, as uneven shades are obtained when it is added all at once. The temperature and duration of dyeing are the same as for the soap or boiled-off liquor bath.

Dyed silk may be after-treated to improve fastness. But if potassium dichromate is used, it should be limited to about one-third of the weight of the dyestuff, since silk is somewhat readily attacked by excess of this salt. Good results are obtained with silk by diazotizing and developing on the fibre.

The direct dyes are used largely for satin, which is a union of silk and cotton, since they provide the easiest method of obtaining a solid shade.

In dyeing silk with direct dyestuffs, the temperature factor must be remembered. Certain of the direct colours have very little affinity for silk at low temperatures, particularly in the presence of sodium carbonate and soap. Others will not dye it at 200° to 212° F. (93.3°–100° C.).

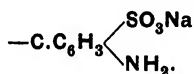
## CHAPTER XXVIII.

### DEVELOPED COLOURS, COUPLED DYES, AND NAPHTHOL DYES.

#### Developed Colours.

A. G. GREEN's discovery of Primuline in 1887 was of great importance from a scientific point of view, for it led to a new method of dyeing, namely, dyeing a fibre with one dyestuff and then changing or developing it into another, which is often superior in some important respects to the original colour.

Primuline when dyed on cotton gives a beautiful yellow colour, but it is very deficient in fastness. The constitution of primuline is very complicated, but it contains an amino group attached to a benzene nucleus (*cf.* p. 382)



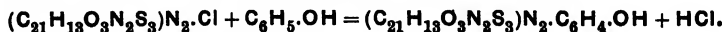
When an organic compound contains primary amino groups attached to an aromatic radical, it gives rise to a diazonium compound on treatment with nitrous acid in the presence of hydrochloric acid; thus, with aniline:



Green found that primuline could be diazotized in exactly the same manner as aniline, as shown in the equation:



The diazotized primuline is a dark-yellow compound, which, like other similar compounds, is very unstable. In itself it would be less useful than the original primuline. But these diazonium compounds react with various phenolic or amino compounds, with the elimination of hydrochloric acid and the formation of a new and more complex substance. This process is termed *coupling*. Now, Green found that when diazotized primuline was coupled with such a body as phenol or  $\beta$ -naphthol, the resulting compound was a new dyestuff, which, although of a different colour from the original primuline, was greatly superior in fastness; the reaction is represented by the equation:



This was an important discovery, and led to the preparation of many other dyestuffs containing amino groups capable of being diazotized on the fibre. The process of coupling the diazotized dyestuff with another suitable compound is termed *developing*, and the amino or hydroxy compounds used for this purpose are known as *developers*. Certain points must be noted: (i) every direct dyestuff containing free amino groups attached to aromatic rings can be diazotized and developed; (ii) the developed colours have generally a different shade or colour from that of the original dyestuff; and (iii) in order to make the



process worth the trouble and expense, the developed colour must have some outstanding property; for example, it must be a colour that cannot be obtained as cheaply by using other dyestuffs, or it must have a greatly increased fastness to light or washing. There are now many direct dyestuffs which are suitable for this kind of after-treatment to produce one or more of the following effects: (a) a new and better colour; (b) a different shade of the same colour; and (c) increased fastness, with but little alteration in shade.

**Developers.**—There are many possible developers, though in practice only a few are used. They all contain either phenolic hydroxyl or amino groups. Either one or both of these may be present, and some contain in addition sulphonic-acid groups. The phenolic developers are dissolved in dilute sodium hydroxide, amino developers in a solution of sodium carbonate, and the sulphonated developers in water. The more common developers are:—

Phenol, carbolic acid . . . . .	$C_6H_5.OH$
$\alpha$ - and $\beta$ -Naphthol . . . . .	$C_{10}H_7.OH$
Resorcinol . . . . .	$C_6H_4(OH)_2$
<i>m</i> -Phenylenediamine . . . . .	$C_6H_4(NH_2)_2$
<i>m</i> -Toluylenediamine, 1-methyl 2:4-diaminobenzene.	$H_3C.C_6H_3.(NH_2)_2$
<i>p</i> -Amino-diphenylamine . . . . .	$C_6H_5.NH.C_6H_4.NH_2$
1:4-Naphthol-sulphonic acid, Neville and Winther's acid.	$C_{10}H_6(OH).SO_3H$
Ethyl- $\beta$ -naphthylamine . . . . .	$C_{10}H_7.NH.C_2H_5$
Naphthylamine ethyl ether . . . . .	$C_{10}H_6(NH_2).O.C_2H_5$

When a dyestuff is diazotized and developed, it does not give the same colour with every developer. On the contrary, each developer generally produces a different colour. In the case of Primuline these developed colours are given in the following table:—

Name of Developer used.	Developed Colour.
Phenol . . . . .	Deeper yellow
$\alpha$ -Naphthol . . . . .	Red
$\beta$ -Naphthol . . . . .	Claret or Maroon
Resorcinol . . . . .	Brown
<i>m</i> -Phenylenediamine . . . . .	Reddish-brown

A particular developer usually tends to give the same colour with different diazotized dyestuffs, and it is, therefore, frequently known by this characteristic colour, which it tends to produce. This is easier for a dyer to remember than a chemical name. These common synonyms are given in the following table:—

Developer.	Synonym.
Phenol . . . . .	Yellow developer
Resorcinol . . . . .	Orange „
$\beta$ -Naphthol . . . . .	Red „
<i>m</i> -Phenylenediamine . . . . .	Brown „
<i>p</i> -Amino-diphenylamine . . . . .	Fast Blue „
1:4-Naphthol-sulphonic acid . . . . .	Crimson „
$\alpha$ -Naphthol . . . . .	Maroon „
<i>m</i> -Toluylenediamine . . . . .	Diamine „
Ethyl- $\beta$ -naphthylamine . . . . .	Claret „

**General Process.**—The general method of applying the developed dyestuffs consists of four different and successive processes, viz.:

- (1) Dyeing the cotton with the original direct dyestuff.
- (2) Diazotizing the dyestuff on the dyed fibre.
- (3) Coupling the diazotized dyestuff with the developer.
- (4) Scouring with warm soap and water to remove any uncombined developer or loosely-attached dyestuff.

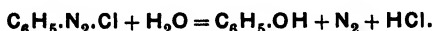
**Dyeing the Cotton.**—Direct dyestuffs suitable for diazotizing and developing are all normal substantive colours, and are dyed on the cotton in the usual manner, in a boiling short bath, with the addition of sodium chloride or sulphate.

The percentage of dyestuff used varies from 2 to 5, according to the depth of the developed colour required. Naturally, the depth of the final colour is determined by that of the original dyestuff fixed on the goods. After dyeing, the goods are washed with water, and placed in the diazotizing bath. But it is not essential that the process should be continued immediately, since azo compounds are very unstable.

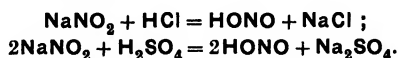
**Diazotizing the Dyestuff.**—In order to ensure complete diazotization certain conditions must be fulfilled. These are—

(a) The bath must contain sufficient free nitrous acid to react with the whole of the dyestuff. The only way to ensure this is to have a slight excess.

(b) The temperature of the bath must be kept low to prevent loss of nitrous acid, and also because the diazonium compounds are decomposed if heated. The maximum temperature permissible is 60° F. (15.6° C.), and, if necessary, in hot weather sufficient ice should be added to the bath to keep the temperature below this point. This is why these colours are sometimes termed *ice colours*. When solutions of diazonium compounds are warmed, nitrogen is evolved and a phenol is formed:



Nitrous acid is not a commercial substance. It is prepared as required by dissolving sodium nitrite in water and adding a solution of diluted hydrochloric or sulphuric acid, or vice versa:



But in order that diazotization may take place, a second molecule of hydrochloric acid is required, as shown by the equation:



Unless sufficient hydrochloric acid is present, the diazonium salt,  $\text{R.N}_2\text{.Cl}$ , cannot be formed. Thus, at least two molecules of hydrochloric acid must be used for each molecule of sodium nitrite. A slight excess of acid does not matter. It is much better than having too little. The quantity of sodium nitrite, and hence of acid, required depends upon the shade of the original direct dyestuff. As a rule, from 1.5 per cent. for light shades rising to 3 per cent. for heavy shades is sufficient. Table LV may be used. A simple bath is 0.5 lb. of sodium nitrite and 0.75 lb. of hydrochloric acid (32° Tw.) for each 10 lb. of cotton.

The vessel used for the diazotizing solution must be of stone or wood. Metal vessels are not only attacked by the acid, but also induce the rapid decomposition of the diazonium compounds. Neither should the solution be exposed to direct sunlight. The volume of water is not very material, since

the chemical action does not depend upon concentration. Sufficient should be used to allow of the goods being worked comfortably in the liquor. From 175 to 200 gallons suffice for 100 lb. of cotton. The required quantity of hydrochloric acid is diluted with the water in the bath, and the sodium nitrite is then stirred in slowly. The salt may, if preferred, be first dissolved in water. Before using, the bath should be tested for free nitrous acid, if it cannot be recognized by its peculiar smell. The following test is very delicate: Some blotting-paper is moistened with a solution of potassium iodide and soluble starch, and dried at a low temperature. When the starch-iodide paper is brought into contact with nitrous acid, iodine is immediately liberated, and this iodine turns the starch blue.

TABLE LV.—COMPOSITION OF DIAZOTIZING BATH.

Percentage of Dyestuff.	Percentage of Sodium Nitrite.	Percentage of Hydrochloric Acid, 32° Tw.	Percentage of Sulphuric Acid, 168° Tw.
0.5	1.0	3.0	2.0
1.0	1.5	3.75	2.5
1.5	1.5	4.5	3.0
2.0	1.75	5.25	3.5
3.0	2.0	6.0	4.0
4.0	2.5	7.5	5.0
5.0	3.0	7.5	5.0

The dyed goods, after rinsing, are worked for about twenty minutes in the cold diazotizing bath. The reaction is very rapid, but there must be complete penetration of the diazotizing mixture. At the end of the twenty minutes the goods are removed from the bath, and rinsed at once in water which has been made faintly acid with hydrochloric or sulphuric acid. About 1 pint of hydrochloric acid to 100 gallons of water is generally sufficient. *The diazotizing bath must contain free nitrous acid at the end of the diazotization.* If it does not, the reaction is incomplete. More sodium nitrite and acid must be added, and the goods put back again immediately. After diazotizing, it is important to observe the following precautions: The goods must not be left lying about or exposed to a strong light or to heat, since these agencies cause the decomposition of the diazonium salts. Careless exposure to light will often cause decomposition of the diazonium salt in patches where the light has impinged on the goods. The dyestuff on these patches cannot be fully developed, and uneven colours result, which cannot be subsequently made right. After rinsing in the acidulated water, the goods must be put into the developing bath at once. If the process cannot be carried to completion, it must not be begun.

*Standing diazotizing baths* are sometimes employed. In such cases about three-quarters of the original quantities of sodium nitrite and acid are added for each successive lot of goods.

**Developing the Diazotized Dyestuff.**—The developers commonly used fall into four classes: (i) simple phenols, which are dissolved in sodium hydroxide solution; (ii) amines which are dissolved by the aid of sodium carbonate; (iii) amines which are dissolved in hydrochloric acid; and (iv) developers soluble in water.

*Naphthols* are dissolved by stirring to a paste with their own weight of

caustic soda solution of 76° Tw. strength, and then adding, with stirring, sufficient boiling water to produce a solution. Phenol and resorcinol are treated in the same manner, but only half their weight of caustic soda solution is used.

*The simple amines*, such as *m*-phenylenediamine and *m*-toluylenediamine, require about one-third of their weight of sodium carbonate,  $\text{Na}_2\text{CO}_3$ , dissolved in boiling water.

*Complex amines*, such as amino-diphenylamine (Fast Blue Developer), are dissolved in about half their weight of hydrochloric acid of 32° Tw.

*Sulphonic-acid developers*, such as 1 : 4-naphthol-sulphonic acid and  $\beta$ -naphthol-sulphonic acid, can be dissolved by water alone.

Table LVI, given by Messrs. I.C.I., Ltd., is useful:—

TABLE LVI.—USE OF DEVELOPERS.

$\alpha$ - and $\beta$ -Naphthol.	Phenol.	Resorcinol.	<i>m</i> -Phenylene-diamine.	<i>m</i> -Toluylene-diamine.	Fast Blue Developer P.
1 $\frac{1}{2}$ lb. is stirred into 1 gal. of boiling water containing 1 $\frac{1}{2}$ lb. of caustic soda of 76° Tw., and made up to 4 gal. with boiling water.	1 $\frac{1}{2}$ lb. is stirred into 1 gal. of boiling water containing $\frac{3}{4}$ lb. of caustic soda of 76° Tw., and made up to 4 gal. with boiling water.	1 $\frac{1}{2}$ lb. is stirred into 1 gal. of boiling water containing $\frac{3}{4}$ lb. of caustic soda of 76° Tw., and made up to 4 gal. with boiling water.	1 $\frac{1}{2}$ lb. is dissolved in 4 gal. of boiling water containing 8 oz. of soda-ash.	1 $\frac{1}{2}$ lb. is dissolved in 4 gal. of boiling water containing 8 oz. of soda-ash.	1 $\frac{1}{2}$ lb. is dissolved in 4 gal. of boiling water containing $\frac{3}{4}$ lb. of hydrochloric acid of 32° Tw.

*Quantity of Developer.* From 1 to 1.5 per cent. of the developer is generally required. The developing bath must contain sufficient to enter into combination with the whole of the diazotized dyestuff. It is better to have an excess than too little; but excess of the developer must not be left in the goods, or it will produce stains. Standing developing baths are quite common, three-quarters of the necessary quantity of the developer being added each time they are used. The approximate quantities of some of the common developers for 5 per cent. of dyestuff are—

$\alpha$ - and $\beta$ -Naphthol . . . . .	0.9 to 1 per cent.
<i>m</i> -Toluylenediamine . . . . .	0.75 „ „
<i>m</i> -Phenylenediamine . . . . .	0.75 „ „
Resorcinol . . . . .	0.75 „ „
Phenol . . . . .	0.5 „ „
Naphthylamine . . . . .	1.5 „ „

*Process of developing.* The dissolved developer is diluted with sufficient cold water in which to work the goods (175 to 200 gallons for 100 lb. of cotton). The rinsed goods are worked in this bath for about 20 min. They are then removed, worked with cold water, hydro-extracted, and dried. Washing in a warm or boiling soap liquor prevents the colour from subsequently bleeding by removing any loosely attached dyestuff.

*Shading* is difficult in the case of developed colours. It requires considerable experience to be able to gauge exactly the shade which the dyed fabric will give when developed. Again, while in some cases a complete change is

produced, in others it is comparatively small. In the latter case, the process itself is suitable for shading, or for producing fuller shades than can be obtained with the original dyestuff. This is the case with blacks. The following methods can be used:—

(1) Mixed direct dyes may be used. These may all be capable of diazotization and development, or they may be a mixture of diazotizable and undiazotizable colours.

(2) Mixed developers may be employed, but only those belonging to the same class can be used. One could not, for example, use together developers requiring alkali and acid respectively to dissolve them.

(3) *Topping with Basic Dyestuffs*.—The developed colours can be topped with basic dyestuffs in the same way as the direct colours. This form of treatment (really after-treatment) is often useful for shading, particularly for brightening.

(4) If a direct colour is diazotized, and developed with a compound containing an amino group attached to an aromatic radical, this amino group can in turn be diazotized, and coupled with another developer.

**After-treatment of Developed Colours.**—In addition to topping with basic dyestuffs, the following may be noted: In some cases the diazotized dyestuff is changed into a new compound by treatment with a warm solution of sodium carbonate. After diazotization the cotton is drained, and then worked at about 120° F. (48·9° C.) in a warm solution containing from 2 to 4·5 lb. of sodium carbonate per 100 lb. of cotton. Another similar process, particularly suitable for Primuline, is to treat the diazotized colour with a cold solution of bleaching powder of from 0·25° to 0·5° Tw. strength.

The following dyestuffs are recommended by Messrs. I.C.I., Ltd., for diazotization and development:—

Dye.	Developer.
Primuline . . . . .	$\beta$ -Naphthol
Primuline . . . . .	Phenol
Primuline . . . . .	Resorcinol
Primuline . . . . .	<i>m</i> -Phenylenediamine
Primuline . . . . .	<i>m</i> -Toluylenediamine
Chlorazol brown M . . . . .	$\beta$ -Naphthol
Chlorazol brown M . . . . .	<i>m</i> -Phenylenediamine
Chlorazol brown M . . . . .	<i>m</i> -Toluylenediamine
Chlorazol diazo blue 2B . . . . .	$\beta$ -Naphthol
Chlorazol black BH . . . . .	Developer D
Chlorazol black BH . . . . .	$\beta$ -Naphthol
Chlorazol black BH . . . . .	<i>m</i> -Phenylenediamine
Chlorazol black BH . . . . .	<i>m</i> -Toluylenediamine
Fast blue . . . . .	Developer P
Chlorazol black DV . . . . .	$\beta$ -Naphthol
Chlorazol black DV . . . . .	<i>m</i> -Phenylenediamine
Chlorazol black DV . . . . .	<i>m</i> -Toluylenediamine
Chlorazol black DV . . . . .	Developer D
Chlorazol black SD . . . . .	$\beta$ -Naphthol
Chlorazol black SD . . . . .	<i>m</i> -Phenylenediamine
Chlorazol black SD . . . . .	<i>m</i> -Toluylenediamine
Chlorazol black SD . . . . .	Developer D
Chlorazol black KB extra . . . . .	$\beta$ -Naphthol
Chlorazol black KB extra . . . . .	<i>m</i> -Phenylenediamine
Chlorazol black KB extra . . . . .	<i>m</i> -Toluylenediamine

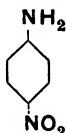
### Coupled Colours.

In producing the developed colours, the direct dyestuff was diazotized on the fibre, and the diazonium compound coupled with a suitable developer. In the case of the *coupled* dyes, this process is reversed. The cotton is dyed with a direct dyestuff containing an amino or hydroxyl group, and the dyed fibre is then treated with a solution of a diazotized base. Direct Brown G (I.C.I.), for example, contains four free amino groups. It dyes cotton a fairly fast brown colour, but a much faster shade can be obtained by coupling it with a solution of diazotized *p*-nitro-aniline.

The process differs from development also in that it is used chiefly to improve shades and fastness, and not to give different colours. In the case of certain blacks and browns it gives an increased depth of shade, accompanied by greater fastness to washing. This applies particularly to the following I.C.I. colours:—

Primuline extra	Chlorazol brown M
Chlorazol fast yellow SGK	„ black DV
„ brown G	„ black E extra
„ brown GM	„ brilliant black BXX

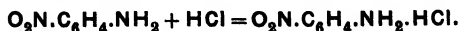
**Para-nitro-aniline** is practically the only base used for coupling. It is a yellow crystalline substance of the composition  $C_6H_4(NO_2)(NH_2)$ , or



It is only sparingly soluble in water. When treated with hydrochloric acid, a hydrochloride,  $O_2N.C_6H_4.NH_2.HCl$ , is formed. This salt dissolves in boiling water or hydrochloric acid, crystallizing out again when the solution is cooled or diluted.

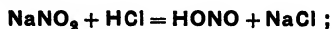
**Diazotization of *p*-nitro-aniline.**—The dyed cotton requires from 0.75 to 1 per cent. of *p*-nitro-aniline as the diazonium salt. Small quantities can be prepared as required, but it is more convenient to have a stock solution. This is made up to contain 2 per cent. of *p*-nitro-aniline. Diazotization is complicated somewhat by the fact that the hydrochloride of *p*-nitro-aniline is practically insoluble in cold water or hydrochloric acid, and, of course, the operation could not be carried out at a high temperature. In order, therefore, to diazotize the base it must be precipitated in the form of minute crystals, and these are treated with the nitrous acid solution. It is very important that the crystals should be very small, in order that they may offer a large surface to the diazotizing mixture. If they are larger, the reaction is very slow, and often incomplete, leaving unchanged *p*-nitro-aniline. The following is a common method of preparing a solution of diazotized *p*-nitro-aniline:—

2 lb. of the base are stirred with 5 pints of hydrochloric acid (32° Tw.) mixed with 5 pints of boiling water. The mixture is boiled and stirred till the base has completely dissolved. The solutions contain *p*-nitro-aniline hydrochloride:



When the base is completely dissolved, 6 gallons of cold water are added, with constant stirring. This causes the precipitation of the *p*-nitro-aniline hydrochloride in very small crystals. The mixture is cooled down to 60° F.

(15.6° C.). In hot weather, or if time is important, 5 lb. of ice may be added. When the temperature reaches 60° F. (15.6° C.), but not before, 1 lb. 2 oz. of solid sodium nitrite is added in one lot, and the mixture well stirred. The reactions which take place are—

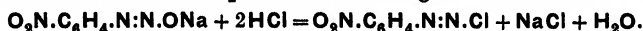


The solution is now diluted with cold water to 10 gallons. Since 10 gallons of water weigh 100 lb., the diluted solution contains 2 per cent. of *p*-nitro-aniline as the diazonium salt. The solution is not very stable, but it may be kept for two or three days in a stone or wooden vessel, covered to protect it from the action of light. The temperature must be kept below 60° F. (15.6° C.), by means of ice if necessary. When required for coupling, the necessary volume of this solution is strained through linen or calico into the coupling bath, which will be described presently.

**Nitrosamine Red.**—Diazotization of *p*-nitro-aniline is rather troublesome, especially if small quantities have to be treated. But, on the other hand, unless coupling is done very frequently, it is useless to make up a large volume of the diazonium compound, owing to its instability. To avoid these difficulties, many attempts have been made to put on the market compounds which will give the diazonium salt with greater readiness. Nitrosamine Red is one of these preparations which is very successful in use. It is prepared by the action of sodium hydroxide on the diazonium salt of *p*-nitro-aniline:



This substance is quite stable, and when treated with hydrochloric acid gives a solution of diazotized *p*-nitro-aniline together with sodium chloride:



Some other types of stabilized diazotized bases may be mentioned, viz.:

**Azophors.**—These are made by treating solutions of diazotized bases with excess of sulphuric acid, concentrating *in vacuo* at 45° C., and mixing with sodium sulphate or aluminium sulphate.

**Nitrazole.**—This is *p*-nitro-aniline diazotized in concentrated sulphuric acid, with the addition of sufficient sodium sulphate to change the excess of sulphuric acid into sodium bisulphate.

**Paranil A.**—Azo compounds can be stabilized by a process of condensation with certain aromatic sulphonic acids in acid solution. Thus, *p*-nitro-aniline when diazotized in the presence of naphthalene  $\beta$ -sulphonic acid gives  $\text{O}_2\text{N.C}_6\text{H}_4.\text{N:NO.SO}_3.\text{C}_{10}\text{H}_7$ .

In order to prepare a coupling bath from the above substances, they are dissolved in water, and sodium acetate is added until the liquid no longer turns Congo-red paper blue.

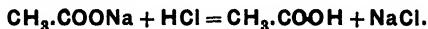
**Application of the Dyestuff.**—The dyestuff is applied in the usual manner for the direct colours, but only selected dyestuffs can be used. In addition to the I.C.I. colours given above, the following also are suitable for coupling:—

Diamine fast violet  
Direct brown G  
Para black R  
Para fast brown GR  
Pyramidol brown  
Direct orange J  
Zambesi black Br

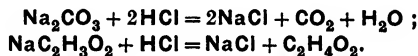
Chicago blue B  
Oxydiamine black N  
Carbon black  
Para bronze NB  
Sultan orange  
Chlorazol red X

After dyeing, the cotton is rinsed, and transferred to the coupling bath.

**Coupling Bath.**—For light shades, about 3·5 gallons of the 2 per cent. stock solution are required for 100 lb. of cotton. For heavy shades, from 5 to 7 gallons are necessary. This is strained into the bath containing sufficient water to enable the goods to be worked easily. The bath will contain free hydrochloric acid, and this prevents the coupling from taking place. A weak acid like acetic does not act in the same way. Hence, immediately before entering the goods into the coupling bath, the free hydrochloric acid is replaced by acetic acid. This is done by adding sodium acetate to the bath, when the following reaction takes place:—



For each part of *p*-nitro-aniline (after diazotization) used, about five parts of sodium acetate are necessary; that is, 1 gallon of the 2 per cent. solution would need about 1 lb. of sodium acetate. It is safer to use rather more (say 1 lb. 1 oz.), to ensure complete freedom from hydrochloric acid. The bath should be tested before use by means of Congo-red paper. This is turned blue by mineral acids, such as hydrochloric, but is not affected by dilute acetic acid. If a positive reaction is obtained, more sodium acetate must be added. Sometimes the hydrochloric acid is partly neutralized with sodium carbonate to save expense. Sodium carbonate has a greater neutralizing power than sodium acetate; this is seen from the equations:



These show that 106 parts of sodium carbonate neutralize 71 of hydrochloric acid, while 82 of sodium acetate neutralize only 36·5. Hence 53 parts of sodium carbonate are equivalent to as much as 82 parts of sodium acetate. Thus, instead of using 1 lb., one might use only 4 oz. of sodium acetate, and from 4½ to 5 oz. of sodium carbonate.

The goods are worked in the cold coupling bath for about 30 min., ice being used if necessary, and they are then washed with cold water.

**After-treatment.**—The fastness of the coupled colours is improved in many cases by after-treatment with salts of copper. But a separate bath is not necessary; the copper salt can be added to the coupling bath. In either case about 1 lb. of copper sulphate is used for 100 lb. of cotton. For a separate bath the goods are worked in a solution of the copper sulphate at about 160° F. (71·1° C.) for 15 min.

Coupled dyes may also be topped with basic dyestuffs, the process increasing both the fastness and the brilliancy of the shade. The process may be carried out in the usual manner in a cold bath in the presence of acetic acid, or from 0·12 to 0·25 per cent. of the dyestuff may be added to the coupling bath. In this case the goods are soaked for a short time in the diazotized *p*-nitro-aniline solution first. They are then lifted, and the dissolved basic dyestuff is added, after which the goods are returned to the bath.

The cotton may be dyed with mixtures of direct colours, all or some of which are capable of being coupled with *p*-nitro-aniline.

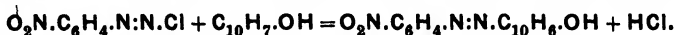
**Use.**—The coupled dyestuffs are not so extensively used as the developed colours, but they find some application in the production of fast browns. The coupling may alter or only deepen the colour, but the new colours have good fastness to washing, fulling, and acids. The following are a few illustrations.



Dye.	After coupling.
Chlorazol brown M . . .	Deeper brown
Chlorazol brown GM . . .	Deeper brown
Chlorazol brilliant black BXX .	Black
Pyramine orange 3G . . .	Brown-orange
Oxamine blue BG . . .	Full green
Oxamine red . . .	Claret
Oxamine maroon . . .	Dark red-brown

### Naphthol or Insoluble Azoic Colours.

In the production of both the developed and the coupled colours, the fibre is first dyed with one dyestuff, which is then changed to another on the fibre. In the case of naphthol colours, although the process is in many respects similar, the dyestuff is actually built up upon the fibre from an intermediate by the introduction of a chromophore. The process is in fact similar to that used by the dyestuff manufacturer. But these azoic colours cannot be obtained commercially, since they are all insoluble in water. The naphthol colours, as the name implies, are made from naphthol by coupling it with a solution of a diazotized base, such as *p*-nitro-aniline. The most important of these colours is para-nitro-aniline red, or "para red," used as a substitute on cotton for the more expensive Turkey red. It is made by impregnating the cotton with  $\beta$ -naphthol, then drying and treating it with a solution of diazotized *p*-nitro-aniline. The reaction is expressed by the equation:



The azoic colours, being insoluble in water, are very fast to washing, but, owing to the fact that they are formed on the fibre by precipitation, are liable to rub. Not only are the azoic colours insoluble in water, but they are not stripped by boiling dilute solutions of acids and alkalis. They can be dissolved from the fibre by boiling pyridine, benzene, or chloroform, and, like indigo, can be volatilized by heat. Formerly, cotton was extensively dyed red by the Turkey-red process, described under the mordant dyestuffs. This is very troublesome and expensive, involving sometimes as many as fifteen different processes. The discovery of para red was therefore welcomed, and this simpler method of dyeing has to a considerable extent displaced the complicated Turkey-red process.

**Para-nitro-aniline Red, "Para Red."**—This colour is fast to washing, fulling, dilute acids or alkalis, and weak bleaching-powder solution, but not very fast to light. It is very useful when a red is required on cotton which does not bleed and which will stand moderate bleaching. The dyeing, however, requires considerable experience, or uneven or loosely-combined colours result. The dyeing consists of several distinct processes, and is used only for yarn.

**Preliminary Scouring.**—It is essential that the cotton should be perfectly permeable. In order to ensure this, the yarn is boiled with sodium hydroxide or carbonate, and washed thoroughly with water.

**Impregnating with  $\beta$ -Naphthol.**—This process is generally termed *paddling*. Cotton has no affinity for  $\beta$ -naphthol; hence it must be saturated with a solution of this substance. Now  $\beta$ -naphthol is comparatively insoluble in water, but dissolves in solutions of sodium hydroxide. In practice, therefore, the cotton is padded with a solution of  $\beta$ -naphthol in sodium hydroxide. But if it were put straight into the developing bath, the  $\beta$ -naphthol would be dissolved out, and the dyestuff precipitated in the bath as well as on the fibre.

To avoid this the padded cotton must be carefully dried. Herein lie the chief difficulties of the process. The para red can be produced only where the  $\beta$ -naphthol is. If this is deficient in quantity, the shade is too light; while if it is distributed unevenly, the colour is patchy. There are other difficulties also, which will be noted as they arise. The  $\beta$ -naphthol solution is applied either by jiggers, by padding machines, or by hand. In order to assist penetration, Turkey-red oil is commonly added to the padding solution. After padding, the cotton must be wrung out evenly.

For 100 lb. of cotton, from  $2\frac{1}{2}$  to  $2\frac{1}{2}$  lb. of  $\beta$ -naphthol are dissolved in the same weight of caustic soda solution of  $75^\circ$  Tw. From 5 to 7 lb. of Turkey-red oil are added, and the mixture made up to 10 gallons with boiling water. When impregnating cotton yarn, it is best to treat small lots of 2 lb. at a time. The excess liquor is squeezed back into the bath, and more added as required. The padding solution contains the sodium salt of  $\beta$ -naphthol,  $C_{10}H_7\cdot ONa$ . When a solution of this salt is exposed to air, it becomes brown in colour; hence the padding solution cannot be kept indefinitely, but should be prepared freshly each time it is required. The importance of even padding cannot be overestimated. Faults made here can never be rectified subsequently.

The following is another formula for padding given by the Badische Anilin- und Soda-Fabrik: The padding solution is made with 1.5 lb. of ground  $\beta$ -naphthol, 1.5 lb. of  $75^\circ$  Tw. caustic soda solution, and 5.25 lb. of 5 per cent. Turkey-red oil, diluted to 7.5 gallons. If a bluish shade is required, the quantities of  $\beta$ -naphthol and caustic soda are increased to 1 lb. 14 oz. The saturation of the yarn is carried out as follows:—

At first  $3\frac{1}{2}$  gallons of the naphthol solution are placed in a wooden or enamel vessel; about 2 lb. of yarn is taken on a rod, and turned four or five times in the liquid. It is then wrung slightly twice, and laid aside on a clean, dry horse. Now add to the bath  $\frac{1}{2}$  gallon more of the liquor, and treat the next 2 lb. of yarn in the same way, the process being repeated till all the yarn has gone through. Then repeat the entire process, taking the hanks in the order in which they were done before, using the old impregnating liquor without any further additions. Each lot is given a few turns, wrung slightly twice, hydro-extracted, and stretched before drying. Hydro-extracting is sometimes replaced by wringing only. The advantage of hydro-extraction, however, is that it is easier to leave the same quantity of naphthol solution in successive lots of goods, and the production of even shades depends very largely upon this.

Messrs. Leopold Cassella & Co. recommend the following padding solution for 100 lb. of cotton (Knecht, Rawson and Loewenthal, *A Manual of Dyeing*, 9th ed., 2, 679: Griffin & Co.): One of the following is weighed out: (a) 1000 g. of  $\beta$ -naphthol; or, for a more bluish red, either (b) 1000 g. of Naphthol RC (Cassella) or (c) a mixture of about 900 g. of  $\beta$ -naphthol and 100 g. of 2:7-naphthol-sulphonic acid (F acid). The naphthol is mixed with 1000 g. of  $75^\circ$  Tw. caustic soda solution, and dissolved by the addition of 10 litres of boiling water. 2500 g. of Turkey-red oil or castor-oil soap are dissolved separately in 10 litres of boiling water. This is mixed with the naphthol solution, and the mixture diluted to 60 litres with water. In padding, 15 litres are put into the bowl at a temperature of  $45^\circ$  C. Two pounds of yarn are passed through. Then 900 ml. more liquor is added, and another 2 lb. of yarn introduced. This is continued.

*Drying the Padded Cotton.*—The prepared hanks must be dried. If they are allowed to lie exposed to air or light, they become brown, and the final colour is affected. The drying demands great care. There is a natural tendency for the  $\beta$ -naphthol solution to percolate downwards and accumulate

in the lower portions of the hanks. Centrifuging helps to prevent this. It should be done twice, packing the goods in the opposite way the second time; they must never be touched with wet hands. The hanks are also reversed several times during drying, or placed on revolving frames in the drying chamber. Also, the hanks should be hung loosely.

The tendency to browning increases with the temperature. The maximum temperature permissible is 140° F. (60° C.). During drying the goods should be carefully protected from light and the action of acid fumes or chlorine. There must be continuous and regular circulation of air, and the damp air must be drawn off. If, after drying, the yarn has a streaky appearance, faulty impregnation or drying is indicated.

*Developing the Dried Cotton.*—The diazotized *p*-nitro-aniline solution is prepared in the same way as for the coupled colours. The temperature of the bath must be kept below 60° F. (15·6° C.). Free hydrochloric acid inhibits the reaction, as does also free caustic alkali. The bath must, therefore, be neutralized with sodium acetate. Sodium hydroxide may be used to neutralize the bath, provided that it is not added in excess. Its use gives the cotton a yellowish shade compared with that obtained when sodium acetate is employed. For coupling, the stock solution of diazotized *p*-nitro-aniline is diluted with about ten times its volume of water, and the goods are worked in this for 20 min. It is, of course, essential that they should be coupled directly they are dry. The coupling may be carried out with small lots successively, just like the padding. For example, 1 gallon of the *p*-nitro-aniline liquor is diluted with 1 gallon of water, and 2 lb. of yarn is worked in the mixture, and wrung out. Then another pint of diazotized liquor is added, and the next 2 lb. of yarn entered.

After coupling, the yarn is washed with water, and then worked for 15 min. at 140° F. (60° C.) in a 0·5 per cent. solution of soap in water. A bluer shade is obtained if a mixture of sodium carbonate (2 parts), Turkey-red oil (18 parts), and water (100 parts) is used instead of soap and water.

*Use of Nitrosamine Red.*—The diazotized *p*-nitro-aniline solution may be prepared directly from Nitrosamine Red. The following formula may be used: When 1 lb. 8 oz. of  $\beta$ -naphthol is used in the B.A.S.F. method described above, there are required 6 lb. 12 oz. of nitrosamine-red paste, 2 lb. 8 oz. of 32° Tw. hydrochloric acid, and 2 lb. 4 oz. of sodium acetate, made up to 7½ gallons with water. If the stronger padding mixture containing 1 lb. 14 oz. of  $\beta$ -naphthol is used, then the quantities for 7½ gallons are 8 lb. 2 oz. of nitrosamine-red paste, 3 lb. of hydrochloric acid, and 2 lb. 12 oz. of sodium acetate. The nitrosamine red is stirred with water, and the hydrochloric acid added slowly. When solution is complete, the sodium acetate, previously dissolved in water, is added with stirring.

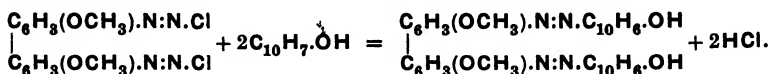
After coupling, each lot of cotton must be washed with water at once to remove excess of the *p*-nitro-aniline or unchanged naphthol. The goods are then passed into a soap-bath at 140° F. (60° C.) containing about half a pound of soap to each 10 gallons of water. After turning about six times, they are washed first with warm, and finally with cold, water. If, before finally drying, the cotton is passed through a further bath containing for each 10 gallons 2 lb. of 5 per cent. Turkey-red oil and from 3 to 4 oz. of sodium carbonate, a bluer shade can be produced.

*After-treatment.*—Para-nitro-aniline Red is changed to brown by salts of copper, and brown shades are obtained in this way by passing the dyed cotton through a dilute boiling solution of copper sulphate. This colour is known as *para-nitro-aniline brown*; but it is better to add the copper sulphate to the

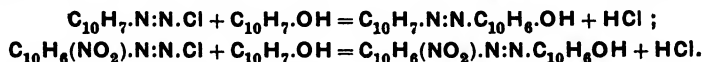
padding liquor. If a copper salt is mixed with sodium hydroxide and  $\beta$ -naphthol, a precipitate of copper hydroxide is produced. But if some substance such as glycerin or tartaric acid is present, the hydroxide is not precipitated. A suitable padding mixture for para-nitro-aniline brown can be made in this way.

**Other Azoic Colours.**—Certain other diazotized bases, besides *p*-nitro-aniline, are occasionally used.

*Dianisidine Blue* is obtained by padding the cotton with  $\beta$ -naphthol and coupling with diazotized dianisidine,  $\text{H}_2\text{N} \cdot (\text{CH}_3\text{O})\text{C}_6\text{H}_3 \cdot \text{C}_6\text{H}_3(\text{OCH}_3) \cdot \text{NH}_2$ . The original colour is violet, but after-treatment with copper salts changes it to a fast blue. The reaction is

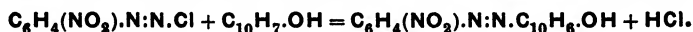


*Sudan CB* consists of  $\beta$ -naphthol coupled with either diazotized  $\beta$ -naphthylamine,  $\text{C}_{10}\text{H}_7 \cdot \text{NH}_2$ , or nitro- $\beta$ -naphthylamine,  $\text{C}_{10}\text{H}_6(\text{NO}_2) \cdot \text{NH}_2$ . In the former case a scarlet, and in the latter a pink, colour is obtained. The reactions are



*$\alpha$ -Naphthylamine Claret*, *Naphthylamine Bordeaux*, is dyed by coupling cotton padded with  $\beta$ -naphthol with diazotized  $\alpha$ -naphthylamine,  $\text{C}_{10}\text{H}_7 \cdot \text{N} : \text{N} \cdot \text{Cl}$ .

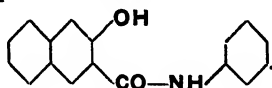
*Meta-nitro-aniline Orange* is obtained when cotton padded with  $\beta$ -naphthol is coupled with diazotized *m*-nitro-aniline,  $\text{C}_6\text{H}_4(\text{NO}_2) \cdot \text{N} : \text{N} \cdot \text{Cl}$ . A stabilized form of diazotized *m*-nitro-aniline is sold as *Azophor Orange*. It consists of a mixture of the diazotized base with aluminium sulphate. The reaction is



There are many other possible combinations, but beyond para red they have no great practical importance. The following table gives some of the other combinations of  $\beta$ -naphthol with diazotized bases, together with the colour obtained:—

Diazotized Base.	Colour.
Benzidine . . . . .	Puce-brown
Tolidine . . . . .	Puce-brown
$\beta$ -Naphthylamine . . . . .	Blue-red
Aminoazobenzene . . . . .	Blue-red

**Naphthol-AS Colours.**—The chief difficulty in dyeing the naphthol colours is that cotton has no affinity for  $\beta$ -naphthol, and the latter must be dried into it. The drying, as has been noted, must be very carefully carried out, and even when the greatest care is taken it is not easy to obtain level results. The application of these azoic colours was greatly simplified by the discovery of a substituted naphthol, termed *Naphthol AS*, by the Griesheim Elektron AG. of Frankfurt-on-Main. Naphthol AS is the anilide of 2-hydroxy-3 naphthoic acid ( $\beta$ -oxynaphthoic acid),  $\text{C}_{10}\text{H}_6(\text{OH}) \cdot \text{COOH}$ , and has the formula  $\text{C}_{10}\text{H}_6(\text{OH}) \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ , or



Its importance lies in the fact that it has a direct affinity for cotton. Drying after padding is thus rendered unnecessary. After working in the

naphthol-AS solution and wringing, the cotton can be transferred at once to the coupling bath. Time is thus saved, and the trouble of uneven drying or oxidation is avoided.

Naphthol AS was soon followed by other similar products, the following table giving the most important:—

Designation.	Arylide of $\beta$ -Oxynaphthoic Acid.
AS . . .	Anilide
AS-BS . . .	<i>m</i> -Nitro-anilide
AS-RL . . .	<i>p</i> -Anisidide
AS-BO . . .	$\alpha$ -Naphthylamide
AS-SW . . .	$\beta$ -Naphthylamide
AS-TR . . .	5-Chloro-2-toluidide
AS-D . . .	<i>o</i> -Toluidide
AS-BR . . .	Dianisidide
AS-BG . . .	Dianisidide

The Griesheim firm make also a series of selected bases suitable for coupling with these naphthol derivatives. These are—

Name of Base.	Constitution.
Fast orange G . .	<i>m</i> -Chloraniline
„ yellow G . .	<i>o</i> -Chloraniline
„ orange GR . .	<i>o</i> -Nitro-aniline
„ scarlet GG . .	2, 5-Dichloraniline
„ scarlet G . .	<i>p</i> -Nitro- <i>o</i> -toluidine, 2-amino-4-nitrotoluene
„ scarlet R . .	<i>m</i> -Nitro- <i>o</i> -anisidine, 1-methoxy-2-amino-3-nitrobenzene
„ scarlet B . .	$\beta$ -Naphthylamine
„ red 2G . .	<i>p</i> -Nitro-aniline
„ red GL . .	<i>m</i> -Nitro- <i>p</i> -toluidine, 3-nitro-4-aminotoluene
„ red 3GL . .	2-Nitro-4-chloraniline
„ red R . .	Chloranisidine
„ red RL . .	2-Amino-5-nitrotoluene
„ red B . .	<i>p</i> -Nitro- <i>o</i> -anisidine, 1-methoxy-2-amino-4-nitrobenzene
„ red BB . .	<i>o</i> -Anisidine
„ red KB . .	2-Amino-4-chlorotoluene
„ red TR . .	2-Amino-5-chlorotoluene hydrochloride
„ garnet G . .	<i>o</i> -Amino-azotoluene, 2-amino-4-methyl-azobenzene
„ corinth B . .	Benzidine
„ maroon B . .	$\alpha$ -Naphthylamine
„ dark blue B . .	<i>o</i> -Dianisidine
„ dark blue R . .	<i>o</i> -Tolidine
„ black LB . .	<i>o</i> -Phenetidine-azo- $\alpha$ -naphthylamine

**General Method for Naphthol-AS Colours.**—The process used in applying these is as follows: Before dyeing, the goods are boiled with a solution of sodium hydroxide or carbonate. After washing and hydro-extracting, they are transferred to the padding bath. Hanks of yarn are worked by hand in 2-lb. lots, being passed through the bath either once or twice according to the nature of the yarn. Thus when the yarn has much twist, it is treated twice with the padding solution. The padded goods are then thoroughly hydro-extracted, the fastness to rubbing of the final colour depending upon the thoroughness of this operation. The padded yarn must not be allowed

to come into contact with copper. If the hydro-extractor is made of this metal, the cotton should be wrapped in cloth. The hydro-extracted padded cotton must be dyed as soon as possible, and must not be exposed to light in the interval between the two processes. It is worked in the coupling bath for about 20 min., then rinsed, and scoured, as usual, with soap and water. Mercerized cotton has a greater affinity for naphthol AS than ordinary cotton, and for this reason a weaker solution of the naphthol is used for these goods.

*Preparation of Naphthol Solution.*—The naphthol AS is stirred into a paste with sodium hydroxide solution and Turkey-red oil. Boiling water is then added, and the mixture boiled till a clear solution is obtained. This is cooled, and formaldehyde is added. It is essential that the solution should be cold before making this addition, for if formaldehyde is added when the solution is hot a precipitate is produced. The mixture is then made up to a suitable volume and used as a stock solution. A liquor must never be heated above 30° to 50° C. after the addition of formaldehyde. The quantities used depend upon the shade required. Table LVII gives the most suitable quantities for dyeing light, medium, and heavy shades on 100 lb. of dry cotton.

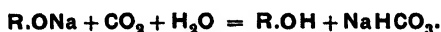
TABLE LVII.—COMPOSITION OF NAPHTHOL-AS SOLUTIONS.

For 100 lb. of Cotton.	Light Shade.	Medium Shade.	Dark Shade.
Naphthol AS . . . . .	390 g.	580 g.	900 g.
Caustic soda, 34° Bé. (61·6° Tw.)	640 ml.	960 ml.	1500 ml.
Turkey-red oil. . . . .	800 ml.	1200 ml.	1875 ml.
Formaldehyde, 30 per cent. .	280 ml.	450 ml.	675 ml.
Final volume after dilution .	64 litres	64 litres	64 litres

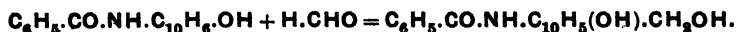
*Padding.*—The padding vessel is charged with 15 litres of the solution and 5 litres of water. After each lot of 2 lb. has been passed through the bath, 1 litre of the naphthol solution is added. If wet boiled-off yarn is treated, the padding solution is diluted to only 32 instead of 64 litres for each 100 lb. The bath in this case is charged, at first, with 7·5 litres of the liquor and 12·5 litres of water, half a litre of the naphthol solution being added after treating each 2 lb. of yarn.

The Turkey-red-oil assists the penetration of the liquor. Other wetting agents which act in alkaline solutions, such as perminal, may be used.

The formaldehyde increases the affinity of the  $\beta$ -naphthol derivative for the cotton, but also protects the treated hanks from *fading*, i.e. loss of coupling power, during exposure to air. This is due to carbon dioxide, which acts in two ways: by combining with sodium hydroxide it reduces its concentration and promotes hydrolysis of the arylide; and by direct action it decomposes the latter; thus:

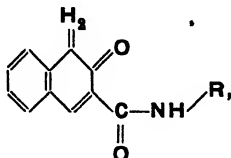


According to Rath (*J. Soc. Chem. Ind.*, 1934, 53, 420) the formaldehyde unites directly with the arylide in the following manner:

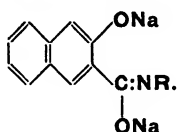


This is the first step in the formation of an artificial resin. When this compound is heated, further changes take place, and an insoluble resin is produced.

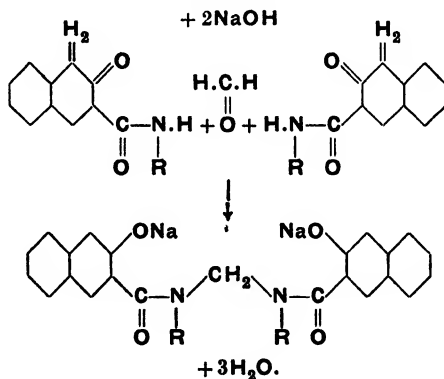
This explains why the bath must not be heated after adding the formaldehyde. The compound is decomposed in the coupling bath, giving formaldehyde and  $\beta$ -oxynaphthoic acid. Higgins (*J. Soc. Dyers Col.*, 1927, 43, 213) gives another explanation, viz. that fading on exposure of the hanks to air is due to the carbon dioxide promoting the formation of a non-coupling arylide, which has the keto form,



the coupling sodium salt having the enolic structure,



It has been suggested further that the formaldehyde hinders the change from the coupling enol to the non-coupling keto form by reacting in the following manner in the presence of sodium hydroxide:



The rate of exhaustion of the naphthol AS depends upon (i) the temperature of the solution, (ii) the period of immersion of the cotton, (iii) the concentration of the naphthol-AS solution, (iv) the ratio of the volume of the solution to the weight of the cotton, and (v) the proportion of salt.

The substantivity of naphthol AS decreases generally with rise of temperature, whilst salt tends to increase it. The amount of naphthol AS absorbed from a concentrated solution is proportionately less than it is under the same conditions from a weaker solution, the highest value of the substantivity existing under those conditions which ensure complete saturation of the cotton.

**Coupling Bath.**—As an example of the usual process Fast Orange G base may be taken. The solution of the diazotized base is made in the following manner: 2600 g. of the Fast Orange G base are mixed with 5.5 litres of hydrochloric acid of 20° Bé. (32° Tw.) and 20 litres of water. To this mixture

are added 50 litres of cold water and 10 kg. of ice. A solution of 1.5 kg. of sodium nitrite in 5 litres of cold water is then added in a fine stream with constant stirring, and the solution is diluted to 100 litres with cold water. This serves as a stock solution of the diazotized base. It is diluted for use to an extent depending on whether the goods are worked by hand or by machine (Table LVIII).

TABLE LVIII.—COUPLING SOLUTIONS (FAST ORANGE G) FOR  
NAPHTHOL-AS DYEING.

	For Hand Working (A).	For Machine Working (B).
Diazotized base solution . . .	60 litres	45 litres
Water . . . . .	40 litres	55 litres
Sodium chloride . . . . .	5 kg.	5 kg.
Sodium acetate . . . . .	1.5 kg.	1.2 kg.
Total volume . . . . .	100 litres	100 litres

The coupling bath is started with 5 litres of solution *A*, 24 litres of water, and 1.5 kg. of NaCl. After coupling each 2 lb. of cotton, 500 ml. of solution *A* are added. In the case of machine working, the initial bath contains 6.5 litres of solution *B*, 22 litres of water, and 1.25 kg. of salt. After passing each 2-lb. lot through, a further 750 ml. of solution *B* are added. But the coupling may also be carried out in one lot in an open bath, larger lots being treated at once. In this case the bath is charged with 85 litres of solution *A*, 900 litres of water, and 45 kg. of salt. This serves for the first 100 lb. For each subsequent lot of 100 lb. there are added to the bath 24 litres of solution *A*, 74 litres of water, and 3.75 kg. of salt.

In some cases aluminium sulphate is added to the diazotized base as a stabilizer. Fast Red GL base is an example. In making the coupling bath 3 kg. of the base are made into a paste with 4 litres of hot water, and 1.5 kg. of sodium nitrite added. The mixture is heated till it becomes clear. It is then cooled, and added gradually to a solution of 5 kg. of aluminium sulphate and 6 litres of hydrochloric acid (32° Tw.) in 80 litres of cold water. After the mixture has been stirred for some time and allowed to stand for half an hour, it is diluted to 100 litres with water. The two solutions, *A* and *B*, are made up as in Table LIX. These solutions are used for coupling in the same way as described for the Fast Orange base.

TABLE LIX.—COUPLING SOLUTIONS (FAST RED GL) FOR  
NAPHTHOL-AS DYEING.

	Solution A.	Solution B.
Diazotized base solution . . .	60 litres	45 litres
Water . . . . .	40 litres	55 litres
Salt . . . . .	5 kg.	5 kg.
Ground chalk . . . . .	1.2 kg.	0.9 kg.



**Soaping.**—When coupling is complete, the goods are washed with water, which may contain a little hydrochloric acid. After this, they are washed again with water containing a little sodium carbonate, and then soaped at 100° C. Soaping removes particles of loosely-attached dyestuff, and develops the full shade. According to Blackshaw (*Dyer and Calico Printer*, 1931, p. 607) the most important factor in soaping is the maintenance of temperature. The bath should be boiling, and the material should be given as much mechanical treatment as possible. But over-soaping must be avoided, since it tends to cause a defect known as *blinding*. Rowe (*J. Soc. Dyers Col.*, 1926, 42, 207) found that, whilst the pigment should be uniformly distributed throughout the fibre, forming in fact a colloidal solution, over-soaping causes it to coagulate into aggregates of particles disseminated through the fibre. These can be seen by microscopic examination. Blackshaw (*loc. cit.*) confirms this view, and states that, in order to obtain maximum fastness to rubbing and full development of shade, the aggregation of particles must proceed to a certain point but no farther. If aggregation goes beyond this point, the colour particles begin to wander or drift to the outside of the cotton fibre, with the result that a surface pigment is formed which will rub off fairly easily. The illustration (Fig. 184) is taken from Blackshaw's paper.



Fig. 184.—Cotton Fibres ( $\times 750$ ), illustrating the aggregation of colour particles. The dark band on the left is the normal, carefully soaped shade of the 2-chloro-*p*-anisidine of  $\beta$ -oxynaphthoic acid coupled with 4-chloro-*m*-anisidine. The light speckled band on the right is the same soaped dyeing, subjected to a severe alkaline boil. The actual colour crystals can be seen quite clearly.

in the usual manner with the diazotized base. The following details are given for 20 lb. of wool:—

Three pounds of soap and 12 lb. of soda-ash are dissolved in 30 gallons of water, and the solution is boiled until clear. One pound three ounces of Naphthol JWL5 is made into a smooth paste with a little of the soap solution, and passed through a sieve into the soap bath. The mixture is then boiled for 5 min., and made up to 60 gallons with water. The wool is entered at a temperature of 50° C., worked for 30 min., and squeezed or whizzed. It is then passed without delay into the coupling bath. This is made in the usual way, and should not be acid to Congo red. After 30 min. the wool is rinsed with cold water, then soaped for 10 min. at 50° C., washed with water, and dried.

For silk the naphthols are applied in a dilute or slightly alkaline solution containing glycerin.

## CHAPTER XXIX.

### THE SULPHUR OR SULPHIDE DYESTUFFS:

ALL the members of this class of dyestuffs contain sulphur. They are insoluble in water, but dissolve in a solution of sodium sulphide. They are made generally by fusing organic bases with sulphur. It is to these facts that they owe their generic name. Vidal Black was discovered by Vidal in 1893. The importance of this discovery lay in the fact that none of the blacks obtained with the substantive dyes on cotton are really fast, while, next to aniline black, Vidal Black is one of the fastest known for cotton.

**Constitution.**—The constitution of the sulphur dyes is not very clear. By no means every dyestuff which contains sulphur is a sulphur dye. Practically every acid or direct dye contains sulphur in the form of sulphonie-acid groups; many, for example the thiazole colours, including primuline, contain sulphur in other groupings; and methylene blue, a typical basic dye, also contains sulphur. But none of these is a sulphur dye. According to Green, the essential difference between other dyestuffs containing sulphur and the true sulphur dyes is that the latter contain a chain of sulphur atoms. That is, the typical grouping is  $-S-S-$  or  $-S-S-S-$ , the dyestuff itself being represented by the formula  $R-S-S-R$  or  $R-S-S-S-R$ . In this respect the sulphur dyestuffs are similar in some ways to the inorganic polysulphides. Ammonium sulphide,  $(NH_4)_2S$ , readily dissolves sulphur, giving a yellow solution containing ammonium polysulphide, which contains linked sulphur atoms, e.g.  $NH_4-S-S-NH_4$ . Organic sulphides containing linked sulphur atoms are known; for example, chloronitrobenzene reacts with sodium sulphide,  $Na_2S_2$ , in the following manner:—



These linked sulphur atoms are held in a state of only comparatively loose chemical combination, and they may be easily split off. In this respect, also, the sulphur dyestuffs behave like polysulphides. Some of the sulphur can be readily oxidized to sulphuric acid. Some of it is given off as sulphuretted hydrogen when the dyestuff is heated with a strong reducing agent, such as stannous chloride and hydrochloric acid. The latter reaction forms, in fact, a good test for the sulphur dyestuffs, either in the free state or on a fabric. Any dyestuff which, when heated with this mixture, gives off sulphuretted hydrogen, is probably a sulphur dye. The test is carried out as follows:—

A little of the dyestuff is placed in a test-tube, together with some stannous chloride and hydrochloric acid. The top of the test-tube is covered with a piece of filter-paper, which is tied round the side of the tube. A drop of lead acetate solution is then placed on the centre of the paper by means of a glass rod, and the test-tube is heated slowly till its contents begin to boil. In the

presence of sulphuretted hydrogen a black stain of lead sulphide is produced on the paper. If the boiling is continued, this disappears, owing to the formation of colourless lead chloride. But the test is not infallible. Some insoluble mordant dyestuffs are rendered soluble by combining them with sodium bisulphite, and sulphites give sulphuretted hydrogen when reduced with stannous chloride and hydrochloric acid. But they give also sulphur dioxide when treated with hydrochloric acid alone, and this enables them to be distinguished from the sulphur dyes.

**Properties.**—The sulphur dyestuffs are in many respects similar to the substantive dyes, in others they are like vat dyes. Like the substantives, they dye vegetable fibres directly, and combine with basic dyestuffs to form insoluble colour lakes. Also, the depth of shade produced is affected by the presence of salt in the dye-bath, the temperature, and the concentration. Like the substantive dyestuffs, again, they tend to form colloidal solutions; and their fastness is improved by after-treatment with metallic salts. But, unlike the substantive dyes, they are all insoluble or only slightly soluble in water, or a solution of sodium carbonate or hydroxide, though they dissolve in one containing sodium sulphide. They are decomposed by acids, generally with the evolution of sulphuretted hydrogen and the precipitation of an insoluble compound. When exposed to air or the action of oxidizing agents, they are slowly oxidized, with the production of sulphuric acid.

The sulphur dyes resemble the vat dyes in forming soluble leuco compounds when reduced in the presence of an alkali. These, when exposed to air, are re-oxidized to the original colouring-matter. Since sodium sulphide is a reducing agent, it therefore frequently happens that the solution of the dyestuff has a different colour from that of the original substance. Solutions of the leuco compounds of some sulphur dyestuffs can be obtained also with sodium hydrosulphite in the same way as with indigo, and the two can be used together.

Owing to the readiness with which the sulphur dyestuffs give rise to sulphuretted hydrogen, metal vessels are dangerous in dyeing with these colours. The dyestuff does not itself react with metals, but if it has been reduced, black stains may be formed. Moreover, copper cannot be used with sodium sulphide solutions.

**Tendering Effect on Cotton.**—The tinctorial power of sulphur dyestuffs is low, 15 per cent. often being required to produce a full shade. They are used chiefly for cotton. The presence of sodium sulphide in the dye-bath, together with sodium carbonate, makes it difficult to apply them to animal fibres. The colours obtained vary in fastness. Many of the sulphur dyestuffs have an important defect, namely, that they are liable to produce tendering in cotton. This is particularly the case with sulphur blacks. The tendering is developed gradually, when the dyed goods are stored. This is thought to be due to the oxidation of some of the sulphur to sulphuric acid, which converts the cotton into hydrocellulose. C. M. Whittaker and C. C. Willcock (*Dyeing with Coal-tar Dyestuffs*, 3rd edn., London, 1939, p. 104), summarizing work which has been done upon this subject, say that in sulphur blacks the sulphur is present in three forms:—

(1) Mechanically free sulphur, which can be extracted with carbon disulphide.

(2) Readily oxidizable combined sulphur, which is converted into sulphuric acid by heating the dyestuff, by exposing it to air, or by dyeing in the presence of air. This kind of sulphur constitutes from 20 to 25 per cent. of the whole.

(3) Firmly combined, or stable, sulphur, which can be oxidized only by

strong oxidizing agents, which produce complete destruction of the molecule. This amounts to from 50 to 75 per cent. of the whole.

The free sulphur is probably an impurity. It has nothing to do with the tendering, nor does it play any part in the dyeing, except that it must be brought into solution. It is only the readily oxidizable sulphur which causes tendering. The presence of an oxygen-carrier accelerates the change.

Liability to cause tendering may be determined by heating a sample of the dyed cotton side by side with an undyed piece of the same fabric in an oven for an hour at a temperature of about  $140^{\circ}\text{C}$ . At the end of this time the samples are removed, and exposed to the air for some time, in order that they may take up moisture. They are then heated again in the oven for an hour, and the tensile strength tested after exposure to air to regain moisture.

When sulphur dyes are known to be liable to cause tendering, the dyed goods must be after-treated. Two methods are used: either something is added to the fabric to neutralize the sulphuric acid as it is formed; or the loosely-combined sulphur is oxidized to sulphuric acid and washed away immediately after dyeing. For the first method, sodium acetate is often used. If the goods are treated with a solution of this salt and dried without washing, the sulphuric acid is replaced by acetic acid as soon as it is formed, and thus tendering is to a large extent inhibited. For the latter method a bath of potassium dichromate and acetic acid may be employed. The bath is made up with from 1 to 3 per cent. of potassium dichromate and the same quantity of acetic acid. The dyed cotton is worked in this for about half an hour at  $140^{\circ}\text{F}$ . ( $60^{\circ}\text{C}$ .), and then washed thoroughly.

**Dissolving Sulphur Dyestuffs.**—The dyestuff is mixed with its own weight of sodium carbonate, and made into a paste with cold water. Sodium sulphide is then added; about the same weight as that of the dyestuff is generally necessary. The paste is then dissolved by pouring hot water on to it with stirring. If a clear solution is not produced, more sodium sulphide should be added. Sodium hydroxide may be substituted for sodium carbonate. The alkali is added first in order to neutralize any free acid, produced by oxidation, which may be present in the dyestuff. Only soft water should be used, since sulphide dyestuffs form insoluble compounds with salts of calcium or magnesium. If soft water is not available, the hard water should be first boiled with sodium carbonate, and the precipitated hardness allowed to settle, the clear, supernatant water being drawn off for use.

**Assistants.**—Glauber's salt or sodium chloride is used, as with the substantive dyestuffs and in the same proportions. Like the substantive dyes, the sulphur dyestuffs exhaust badly, even in the presence of salt; hence, standing baths are very commonly used. Since alkaline baths are used, soap or Turkey-red oil may be added to assist penetration. From 1 to 2 per cent. is a suitable quantity. Free sulphur sometimes makes its appearance in a sulphur dye-bath. When this happens, sodium sulphite is added till it dissolves; the reaction is



If free sulphur is not redissolved, it sticks to the goods, forming light-coloured patches.

### Application of the Sulphur Dyestuffs to Cotton.

Most of the sulphur dyestuffs will dye cotton from a cold or lukewarm bath, but they are generally used at the boiling-point, though the goods are often allowed to cool off for a time in the dye liquor. The bath is made up in the

following way: The solution of the dyestuff is diluted with about fifteen to twenty times as much water as cotton, i.e. a short bath is used. From 10 to 40 per cent. of salt is added, according to the shade. The cotton is wetted but, and entered at about 140° F. (60° C.). The temperature of the bath is then raised to the boiling-point for about half an hour, the goods being frequently turned. The steam is then shut off, and the goods are allowed to remain in the cooling liquor for from half an hour to an hour. During this time they must be completely covered by the dye liquor. They are at once squeezed or hydro-extracted, and then rinsed, again hydro-extracted, and dried. It is important that excess of dye liquor should be removed as quickly as possible after the goods leave the dye-bath, to prevent oxidation of that still adhering to the fabric and not combined with it.

Whittaker's method for promoting exhaustion may be mentioned (*Dyer and Calico Printer*, 1916, p. 50). It consists in adding, towards the end of the dyeing, about 5 per cent. of ammonium sulphate, formate, or acetate, or the equivalent amount of the free acid. The effect of ammonium salts is gradually to replace sodium sulphide and free alkali by ammonium compounds, thus reducing the solubility of the dyestuff. The addition of acid simply



Fig. 185.—Bent Stick for Sulphur Dyestuffs.

reduces the alkalinity. But care must be taken to maintain the bath alkaline throughout the dyeing.

When dyeing with sulphur dyestuffs, the goods should be kept immersed all the time. Intermittent exposure to air causes the oxidation of leuco-compounds of the dyestuff loosely attached to the surface. These are liable afterwards to rub off easily or bleed. Black piece-goods are often dyed in ordinary jiggers, but the method is not really safe. Hanks are suspended on bent sticks (Fig. 185) so that they are completely immersed in the dye liquor. Hosiery garments may be placed in a cage, which is lowered into the dye-bath, the circulation of the liquor being maintained by a paddle. As soon as the dyeing is complete, the cage is raised, and immediately immersed in a second bath of water, which stands close to it. Special types of rotary drums are also used in which access of air is prevented. Smith's rotating drum for dyeing sulphur-black is illustrated in Fig. 186.

**Standing baths** are commonly used for the sulphur dyestuffs. The strength with respect to dyestuff is maintained by adding about 70 per cent. of the original quantity each time the bath is used. Sufficient sodium sulphide to produce a clear solution and some salt are also necessary. But it is important not to have too great an excess of sodium sulphide, or it will tend to inhibit dyeing. The density of the bath at 60° F. (15.6° C.) should be from 8° to 10° Tw. for blacks and from 4° to 5° Tw. for other colours.

**Estimation of Sodium Sulphide in the Dye-bath.**—This is often useful in the case of standing baths. Sen (*J. Soc. Chem. Ind.*, 1914, 33, 916) recommends the following method: First the sodium carbonate is precipitated by means of barium chloride, and then the dyestuff by adding excess of sodium chloride. The mixture is made up to a definite volume, mixed, and allowed to stand for some time. After the precipitate has settled down, the sodium

sulphide is titrated in a portion by means of standard zinc sulphate solution, using sodium nitroprusside as an external indicator. If the addition of salt does not clarify the solution sufficiently, some pure cotton is added.

**After-treatment of Sulphur Colours.**—It should be noted that very many sulphur colours require *ageing*, i.e. exposure to air, to develop their full shade. This makes it somewhat difficult to match patterns without considerable experience in allowing for the effect produced by atmospheric oxidation. This effect can, however, be accelerated by treating a sample of the dyed fabric with a faintly alkaline solution of hydrogen peroxide.

There are special methods of after-treatment, which are quite similar to those used with the direct colours. The chief of these are—

(1) *Topping with Basic Dyes.*—The sulphur dyestuffs may be topped with suitable basic dyes in just the same way as the substantive colours. From 0.1 to 0.5 per cent. of the basic dye is used, together with from 2 to 5 per cent. of acetic acid. The goods are entered into a cold bath to which the acid has

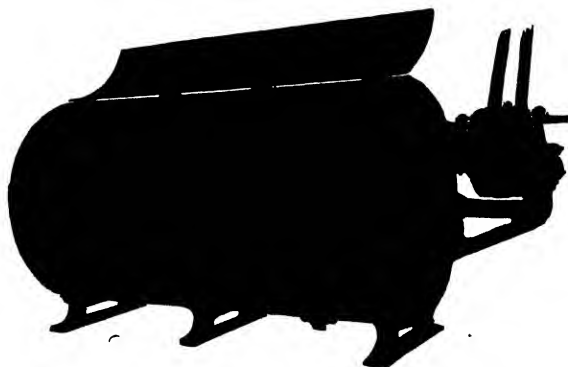


Fig. 186.—Smith Rotating Drum for Sulphur Dyestuffs.

been added, and the dye is added gradually. The temperature may be raised gradually to about 50° C.

(2) *After-treatment with Metallic Salts.*—Copper sulphate and potassium dichromate are chiefly used. The former increases the fastness to light, while the dichromate improves the power of withstanding milling; hence, as with the direct dyes, both are often used together. But copper sulphate is not suitable for blacks or other colours which have a tendency to tendering, since, if left in the goods, it acts as an oxygen-carrier. These processes of after-treatment are carried out in the same way as for the direct colours. The dichromate after-treatment, in the case of blacks, greatly reduces (as already mentioned) the tendency to tendering.

(3) *After-treatment with Hydrogen Peroxide.*—This is used chiefly for blues. The dyed goods are soaked for an hour in a cold bath of dilute hydrogen peroxide made faintly alkaline with ammonia. Ordinary 10- to 12-volume peroxide, diluted with ten times its volume of water, may be used. The vessel must be made of wood or other material which will not act as a catalyst. Sodium perborate is often used instead of hydrogen peroxide, but in this case a warm bath is necessary. After treatment the goods are washed, soaped, and dried.

(4) *After-treatment of Blacks.*—Sulphur blacks, like many others, are liable to have a bronzy shade. This is said to be contributed to by various factors,

such as the use of too much dyestuff, exposure to air during the dyeing, and failing to remove the excess dye liquor immediately after dyeing, or incomplete rinsing, or the use of insufficient sodium sulphide in the dye-bath. This bronziness may often be removed by means of a bath of dilute sodium sulphide solution (e.g. 0.1 per cent., at 30° C.), which redissolves some of the dyestuff from the surface of the goods. Alternatively, a solution containing 3 per cent. of acetic acid and 2 per cent. of sodium chromate on the weight of the goods may be used at 60° C.

A very common way of after-treating blacks is to work them in a bath of olive oil emulsified in soap and water like the direct blacks. A solution of olive-oil soap of about 5 g. per litre strength, containing 1 g. per litre of olive oil, may be used at a temperature of 140° F. (60° C.). Turkey-red oil is sometimes substituted for olive-oil soap, and the soap is occasionally omitted altogether, the olive oil being emulsified by means of a dilute solution of sodium carbonate. Another formula for 100 lb. of dyed cotton is to work it in a bath, at 160° to 175° F. (71.1°–79.4° C.), containing 14 oz. of each of the following: soap, olein, olive oil, and ammonia; while still better results are produced by the further addition of about 5 lb. of Turkey-red oil.

Sulphur blacks are also after-treated, to inhibit tendering, by working them in a dilute (0.5 per cent.) solution of sodium acetate or formate, hydro-extracting, and drying without further washing. Or potassium dichromate and acetic acid may be employed in the way described above.

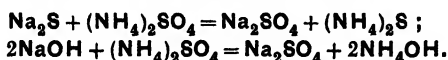
The sulphur blacks, like direct blacks, are often combined with others. Thus they may be topped with aniline black or indigo. These methods will be fully described later. Topping with aniline black adds considerable weight to the dyed goods, giving them a fuller feel. J. M. Matthews (*Application of Dyestuffs to Textiles, Paper, Leather, and Other Materials*, p. 389) gives the following formula: A bath is made containing 4 per cent. of aniline hydrochloride, 6 per cent. of hydrochloric acid (30° Tw.), 3 per cent. of sulphuric acid (168° Tw.), 3 per cent. of copper sulphate, and 4 per cent. of potassium dichromate. The dyed cotton is worked for an hour in the cold bath, after which the temperature is raised slowly to 140° F. (60° C.). The goods are then washed and soaped.

**Uneven Shades.**—The sulphur dyestuffs are, as a rule, level dyers. The colours may be partly stripped from cotton by means of a warm solution of sodium sulphide, and more completely by a solution of bleaching powder.

### Application of the Sulphur Dyestuffs to Wool and Silk.

Animal fibres are difficult to dye with sulphur dyestuffs. Strong alkalis damage the fibres; while weak alkalis do not dissolve the dyestuffs readily, nor hold their leuco compounds in solution. The use of protective colloids, such as glue or starch, has been suggested. If the dye-bath contains about 5 parts of dissolved glue for every 100 of wool, the latter is less liable to alkaline damage. Boiled starch acts in a similar manner. Certain proprietary colloidal solutions, such as "Protectol," are said to protect unions completely from alkaline damage in a sulphur dye-bath, while at the same time keeping the dye off the wool, thus enabling the cotton to be dyed, and leaving the wool merely stained and suitable for cross-dyeing with acid dyestuffs. The addition of glucose to the dye-bath also tends to prevent the damaging of animal fibres by alkali as well as to reduce the dyestuffs to more readily soluble leuco compounds. Twice as much glucose as dyestuff is required, together with some Turkey-red oil.

Vidal Black can be converted into a more soluble form by treatment with a normal or acid alkali sulphite. Lodge (*J. Soc. Chem. Ind.*, 1916, 35, 41) found that this also applies to its leuco compound. The Lodge-Evans patented process is founded on this fact, since these more readily soluble leuco compounds can be dissolved in ammonium sulphide. The leuco compound is first prepared, and dissolved in sodium sulphide. The latter is then changed into ammonium sulphide in the dye-bath by means of an ammonium salt, while free caustic alkali is at the same time changed into ammonia, thus:



In this way a solution of the dyestuff is obtained of sufficient concentration to give any desired shade, but at the same time of such feeble alkalinity as not to damage animal fibres. Thus, as an example, 1 part of the sulphur dyestuff is boiled for from 5 to 10 min. with 2 parts of sodium sulphite and 10 of water. One part of concentrated sodium sulphide is then added, and the mixture kept hot (but not boiled) till the dyestuff is completely reduced. The solution of the leuco compound thus obtained is poured into the dye-bath, which is then heated to the required temperature, and 2 parts of neutralized ammonium sulphate or other ammonium salt are added to remove caustic alkalis and to produce ammonium sulphide. During dyeing the goods are kept beneath the surface of the liquor as much as possible. In the case of unions where the cotton only has to be dyed, the goods should be worked in the cold or lukewarm solution. But if both wool and cotton are to be dyed, the bath is heated to 80° C., the heating stopped, and the goods worked for from 10 to 15 min. They are then squeezed, and put into a cold bath, where they are worked till the cotton has acquired the correct shade. The method may be varied by boiling the dyestuff with sodium sulphide, pouring the solution obtained into the dye-bath at the dyeing temperature (80° C.), and then adding sodium hydrosulphite; ammonium sulphate and ammonia being used to neutralize acidity in the dyestuff and remove caustic alkali from the bath. Lodge regards sodium sulphite as a proper assistant for all sulphide dyestuffs which form leuco compounds, since sulphur or feebly-combined sulphur is always present, as it is also in commercial sodium sulphide. Sulphide colours dyed on wool by this method are fuller and more bloomy than on cotton, and have excellent resistance to washing and milling. Most of them are fast to light if after-chromed. On silk they are still better than on wool.

Sen (*J. Soc. Chem. Ind.*, 1916, 35, 1107) suggests the improvement of Lodge's process by adding a little Turkey-red oil to the dye-bath to assist penetration, and some formic acid towards the end of the operation.

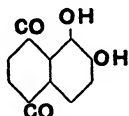


## CHAPTER XXX.

### THE MORDANT DYE STUFFS.

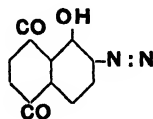
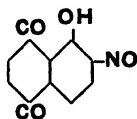
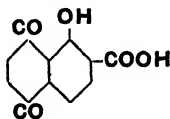
THE members of this class are characterized by the fact that they do not, as a rule, dye any fibre directly, but form insoluble colour lakes with basic hydroxides; hence the fibres are in all cases mordanted with a suitable hydroxide or oxide. The class includes most of the natural dyestuffs, such as logwood, cochineal, fustic, and madder. These natural mordant-dyestuffs are among the oldest known. Logwood and fustic are still used extensively, but, except for special purposes, synthetics have almost entirely replaced the natural mordant dyes.

**Constitution.**—The characteristic auxochrome of this class of dyestuffs is the phenolic hydroxyl group. Kostanecky showed that derivatives of anthraquinone which are dyestuffs contain two phenolic hydroxyl groups in the *ortho* position with regard to each other, and *peri* to one of the carboxyl or ketone groups of the chromophore. Thus the typical grouping of this class is—



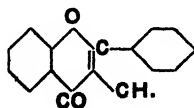
Alizarine, madder, and cochineal all contain this group, and are important mordant dyestuffs. These hydroxyl groups are characterized by their ability to form stable colour lakes with metallic oxides or hydroxides.

If one hydroxyl group has any other position than the *ortho* with regard to the other, the compound has little affinity for mordants. But one of the *ortho* hydroxyl groups may be replaced by a carboxyl, a nitroso, or an azo group, thus giving

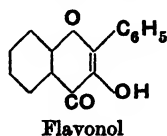
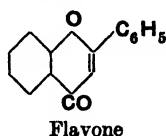


The discovery of the possibility of introducing an azo group extended greatly the possibilities of making artificial mordant dyestuffs. These are known as the *ortho-oxyazo* colours.

Many of the mordant dyestuffs contain the *flavone* grouping,



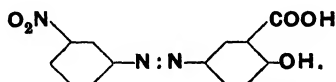
This group of dyestuffs includes many of the natural vegetable mordant colours, such as logwood, fustic, and cutch. They are derivatives of either flavone or flavonol, which are represented by the formulæ



A number of the mordant dyestuffs are members of other dyeing groups as well. Among these are—

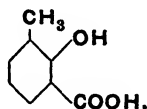
(1) *The Acid Mordant Dyestuffs*.—These have been mentioned already in connection with the acid dyestuffs (p. 361). They contain either sulphonic-acid or carboxyl-groups in addition to the mordant groups, and are often azo compounds.

Thus, if salicylic acid is coupled with *m*-nitraniline, the product is Alizarine Yellow GG,

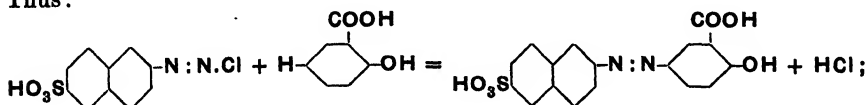


This is already an azo acid dyestuff. It contains a hydroxyl group and a carboxyl group (replacing a second hydroxyl) in the *ortho* position with respect to each other; hence it is capable of forming colour lakes with metallic oxides, and can be mordanted on the fibre or dyed by the metachrome process.

Another example is Anthracene Chrome Yellow, which contains both a sulphonic-acid and a carboxyl group. It is made by coupling diazotized  $\beta$ -naphthylamine-monosulphonic acid (5, 6, or 8) with salicylic acid or *o*-cresotinic acid,

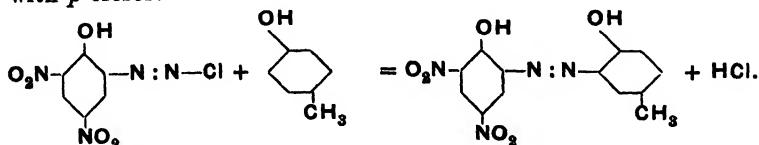


Thus:



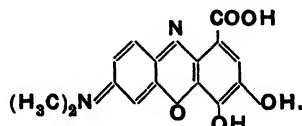
the dyestuff is the sodium salt of this acid.

*The Metachrome Dyestuffs* are similar, but of more complex structure, and do not as a rule contain acid groupings. Metachrome Olive Brown MO (I.C.I.) is a comparatively simple example; it is made by coupling diazotized picramic acid with *p*-cresol:



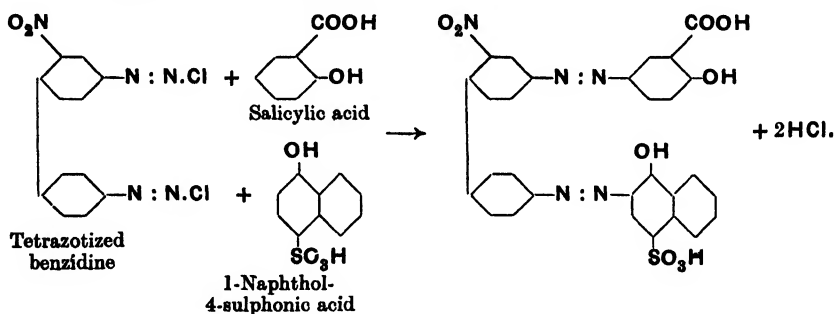
(2) *Basic Mordant Dyestuffs*, such as the gallocyanines, contain amino or substituted amino groups; thus gallocyanine (D.H.) contains the groups  $-OH$  and  $-N(CH_3)_2$ . They dye animal fibres directly, but give faster colours with mordants.

Gallocyanine is made from gallic acid,  $C_6H_2(OH)_3.COOH$ , by heating it with *p*-nitroso-dimethylaniline hydrochloride,  $ON.C_6H_4.N(CH_3)_2.HCl$ , and methyl alcohol till a dark violet-blue colour is obtained, after which the alcohol is distilled off, and the residue evaporated to dryness. This is then boiled with water, and the insoluble gallocyanine filtered off and dried at a low temperature ( $40^\circ$  to  $50^\circ$  C.). The dyestuff forms soluble salts with acids; it has the formula



The Janus dyes have been referred to in dealing with the basic colours.

(3) *Other mordant dyestuffs* have resemblances to the direct dyestuffs, i.e. they dye unmordanted cotton. Salicine Yellow, Salicine Red, and Anthracene Red are examples. The last-named contains hydroxyl, carboxyl, and sulphonic-acid groups, and is also a disazo compound. It is prepared by coupling tetrazotized 2-nitrobenzidine with salicylic acid and 1-naphthol-4-sulphonic acid; the stages of the reaction are:



Certain of the mordant dyestuffs are insoluble in water. These are used in the form of a paste, which is strained into the dye-bath. In some cases they are rendered more soluble by combining them with sodium bisulphite, which is split off in the dye-bath. Solutions of mordant dyes can be identified by the fact that they give insoluble colour lakes when heated with solutions of chromium salts or potassium dichromate. A solution of chromium fluoride containing sodium acetate is a useful reagent for this purpose.

**Application of Mordant Dyestuffs.**—The true mordant dyestuffs all require two distinct operations in dyeing, namely (i) mordanting, and (ii) dyeing.

In mordanting, the goods are either padded, warmed, or boiled with a dilute solution of the mordant, either with or without the addition of an assistant, and then washed. The mordant must be deposited on the fibre slowly and evenly, since its distribution determines that of the colour lake. For this reason also, uneven shades are very difficult to correct. They can often be stripped by boiling the fabrics with dilute oxalic acid (5 per cent.) to decompose the colour lake, and then dissolving the liberated dyestuff in a bath of dilute ammonia. In some cases ordinary stripping agents, such as sodium hydrosulphite or formosul, are suitable.

**Single-bath Process.**—With certain dyestuffs wool can be mordanted and dyed by a single-bath process, by the following method: The bath is prepared

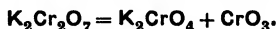
with 1.5 per cent. of potassium dichromate, 3 per cent. of lactic acid, and 1 per cent. of sulphuric acid; the goods are entered at 104° F. (40° C.), the temperature raised to the boil in 30 min., and boiling continued for  $\frac{3}{4}$  to 1 hour. After complete exhaustion the bath is cooled down to 104° to 122° F. (40°–50° C.) and neutralized with ammonia, and the well-dissolved and diluted dyestuff added, with continuous stirring. The bath is then slowly raised to the boil, and after boiling for 30 min. 3 to 5 per cent. of acetic acid is gradually added (see further below).

The metachrome dyestuffs, which are used in a single-bath process, have been mentioned already.

**Mordants and Assistants.**—The mordant is a metallic hydroxide or oxide, which is deposited on the fibre from a solution of one of its salts, and which is capable of forming an insoluble coloured compound with the dyestuff. The mordant must be cheap, give fast colours, and not damage the fibre. The choice, although theoretically large, is in practice rather limited, being confined chiefly to the oxides of aluminium, chromium, copper, iron, and tin. The choice depends also upon the colour required, since many of the mordant dyestuffs are *polygenetic*, i.e. produce different colours with different mordants. Thus, alizarine gives with alumina a red and with oxide of iron a purple colour.

Oxides of chromium are the most important of the mordants, being used very extensively for wool. Two oxides are employed, viz. (i) chromic oxide, chromium sesquioxide,  $\text{Cr}_2\text{O}_3$ , and (ii) chromium trioxide, chromic anhydride,  $\text{CrO}_3$ . Basic chromic oxide,  $\text{Cr}_2\text{O}_3$ , is commonly precipitated on the fibre by boiling the fabric with a dilute solution of potassium dichromate in the presence of a reducing agent, termed an *assistant*. The acid mordant, chromium trioxide, is liberated when potassium dichromate is treated with sulphuric acid alone. The chief assistants are potassium hydrogen tartrate (cream of tartar), formic acid, lactic acid, and oxalic acid. Chromium mordants are not used for cotton, and silk is damaged by treatment with dichromates.

**Mordanting Wool.**—*Mordanting with Chromium.*—The oxidizing mordant, chromium trioxide, is used when dyeing wool with logwood. When wool is boiled with potassium dichromate, this oxide is deposited on the fibre and potassium chromate remains in the solution, as shown by the equation:



If the wool contains alkali, this changes its equivalent of dichromate into chromate:



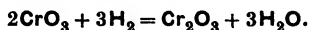
It is evident that mordanting with dichromate alone is wasteful. If, however, an acid solution of dichromate is used, no loss of chromium occurs, since the chromate is changed back into dichromate in accordance with the equation:



The bath is prepared with 3 per cent. of potassium dichromate and 1 per cent. of sulphuric acid on the weight of the wool. The scoured wet wool is introduced into the bath at a temperature not exceeding 140° F. (60° C.). The temperature of the bath is raised slowly to the boiling-point, and boiling continued for from one to two hours, after which the wool is removed and washed. It should have a yellowish colour, and must be dyed at once. If it is kept for any length of time, the chromium trioxide is changed gradually into chromium sesquioxide,  $\text{Cr}_2\text{O}_3$ , owing to oxidation of the wool. This will in turn

give rise to uneven dyeing. It is important that excess of dichromate should not be used, since the epithelial scales of wool are destroyed gradually by strong oxidizing agents. Standing baths of dichromate are used sometimes, more potassium dichromate being added each time they are used.

For mordant dyestuffs other than logwood, wool is mordanted with the basic oxide,  $\text{Cr}_2\text{O}_3$ . This is produced in the mordanting bath from potassium dichromate together with a reducing agent, which acts upon chromium trioxide in accordance with the equation:



The reduction should not take place rapidly, and for this reason a mild reducing agent, such as cream of tartar (potassium hydrogen tartrate), should be used.

The wool is wetted down, and entered at about  $140^\circ \text{F}$ . ( $60^\circ \text{C}$ .) into a bath containing 3 per cent. of potassium dichromate. The temperature is then raised slowly to the boiling-point for half an hour. The goods are then lifted, and 3 per cent. of cream of tartar previously dissolved in water is added to the bath, and stirred in. The goods are returned, and the contents of the bath boiled gently for another half-hour. They are then removed and washed. The mordanted material will have a light-green colour, and in this case immediate dyeing is not of such great importance. Cream of tartar causes a very gradual reduction of the dichromate and hence an even distribution of the mordant. The following reducing agents are cheaper and are frequently used instead: formic acid, lactic acid, and oxalic acid. In these cases the reduction is more complete, and rather less dichromate is necessary. Moreover, it is much more rapid than when cream of tartar is used, and the temperature must be controlled to prevent uneven deposition of the mordant. The details of the method for formic acid are as follows: From 1 to 2 per cent. of potassium dichromate and the same quantity of 85 per cent. formic acid are dissolved in the bath. The wool is wetted down, and entered at about  $140^\circ \text{F}$ . ( $60^\circ \text{C}$ .) After working it for 15 min., the temperature is raised slowly to the boiling-point for half an hour. Lactic acid is used in a similar manner, often with the addition of a little sulphuric acid. About 2 per cent. of potassium dichromate and 5 per cent. of 50 per cent. lactic acid are necessary. If sulphuric acid is employed, half of the lactic acid is replaced by 1 per cent. of sulphuric acid.

Sulphurous acid, or sodium bisulphite, is the cheapest reducing agent to use, but when it is added to the dichromate bath the reduction is too rapid, and the sulphur dioxide is rapidly lost as gas. But it may be used in another way: the goods are first mordanted with chromium trioxide in the manner described above, then immersed in a cold bath containing about 5 per cent. of sodium bisulphite, and finally washed.

Potassium dichromate is sometimes replaced by chromium fluoride,  $\text{CrF}_3$ . From 3 to 4 per cent. of the salt and 1 per cent. of oxalic acid are dissolved in water and mixed, and the wool is boiled in the solution for about an hour.

*Mordanting with Iron.*—Ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , is generally used, with either cream of tartar or oxalic acid as an assistant or reducing agent. From 3 to 5 per cent. of crystalline ferrous sulphate and the same quantity of cream of tartar or oxalic acid are dissolved separately in water, and the solutions mixed in the bath. The wool is wetted down, and entered at  $140^\circ \text{F}$ . ( $60^\circ \text{C}$ .); the temperature of the bath is raised slowly to the boiling-point, gentle boiling being kept up for about an hour. The goods are then washed, and should be dyed at once. They should have a white or creamy tint, due to the deposition of ferrous oxide,  $\text{FeO}$ , on the fibre. If they have a brown or red

tint the ferrous oxide has been oxidized to ferric oxide,  $\text{Fe}_2\text{O}_3$ . The presence of the reducing agent should prevent this change from taking place.

**Mordanting with Tin.**—Stannous oxide,  $\text{SnO}$ , is occasionally used, for example when dyeing Cochineal Scarlet. From 4 to 5 per cent. of stannous chloride and the same quantity of cream of tartar are dissolved in water and mixed. The cream of tartar prevents the precipitation of the basic salt,  $2\text{Sn}(\text{OH})\text{Cl} \cdot \text{H}_2\text{O}$ . The wool is wetted and entered at  $140^\circ \text{F}$ . ( $60^\circ \text{C}$ .), and the temperature of the bath is then raised to about  $190^\circ \text{F}$ . ( $87.8^\circ \text{C}$ .) for an hour. After washing, the goods should be dyed at once, since stannous oxide is oxidized readily to stannic oxide,  $\text{SnO}_2$ .

**Mordanting with Aluminium.**—Either aluminium sulphate or alum may be used. In the presence of wool, a boiling solution of aluminium sulphate is hydrolysed into sulphuric acid and a basic salt, the latter being adsorbed by the wool:

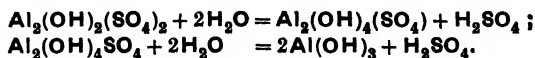


Thus, wool may be mordanted by simply boiling it with a solution of aluminium sulphate or alum. About 3 per cent. of aluminium sulphate or 5 per cent. of alum is required. As a rule, however, about half as much cream of tartar, or oxalic acid, as mordant is also added to the bath. These are dissolved separately in water and mixed. The goods are wetted and entered at  $140^\circ \text{F}$ . ( $60^\circ \text{C}$ .), and the bath then raised to the boiling-point for about an hour.

**Mordanting Cotton.**—Cotton has practically no affinity for basic oxides, and is difficult to mordant. For this reason the mordant dyestuffs are very little used for cotton goods, except for the production of Turkey red, which consists of alizarine dyed on an aluminium mordant. Cotton, unlike wool, cannot be mordanted by boiling it with a solution of aluminium sulphate or alum. Not enough alumina could be fixed on the fibre in this way. But when a basic solution of aluminium sulphate or alum is boiled, it becomes more basic and less soluble in water, the less soluble basic compound being deposited on the cotton; if the cotton is impregnated with a solution of the basic salt and dried, a similar change takes place. The sulphuric acid produced by hydrolysis, however, would also remain in the goods, and cause tendering. To avoid this, the alumina is fixed, and the acid neutralized, by treatment with a mild alkali such as ammonium carbonate, sodium silicate, sodium phosphate, or soap. Aluminium sulphate (or alum) treated with sodium bicarbonate, or other alkali gives the following series of compounds, in which the  $\text{SO}_4$  groups are replaced successively by hydroxyl groups:

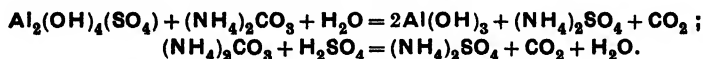
- (1)  $\text{Al}_2(\text{SO}_4)_3 + 2\text{NaHCO}_3 = \text{Al}_2(\text{OH})_2(\text{SO}_4)_2 + \text{Na}_2\text{SO}_4 + 2\text{CO}_2$ ;
- (2)  $2\text{Al}_2(\text{SO}_4)_3 + 6\text{NaHCO}_3 = \text{Al}_4(\text{OH})_6(\text{SO}_4)_3 + 3\text{Na}_2\text{SO}_4 + 6\text{CO}_2$ ;
- (3)  $\text{Al}_2(\text{SO}_4)_3 + 4\text{NaHCO}_3 = \text{Al}_3(\text{OH})_4(\text{SO}_4) + 2\text{Na}_2\text{SO}_4 + 4\text{CO}_2$ ;
- (4)  $\text{Al}_2(\text{SO}_4)_3 + 6\text{NaHCO}_3 = \text{Al}_3(\text{OH})_6 + 3\text{Na}_2\text{SO}_4 + 6\text{CO}_2$ .

When a solution containing a basic sulphate is either boiled, largely diluted, or dried into cotton, hydrolysis takes place, a more basic salt and sulphuric acid being formed, *e.g.*:



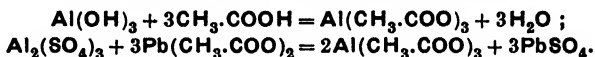
If the solution is allowed to cool, the more basic precipitate again dissolves—that is, the reaction is reversible. But if the cotton is removed from the boiling solution, the precipitated basic compound remains on the fibre. If cotton is boiled in an aqueous 20 per cent. solution of alum, it takes up about

13 per cent. of alumina,  $\text{Al}_2\text{O}_3$ . A solution containing the same quantity of  $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$  begins to give a precipitate at  $68^\circ \text{C}$ . (or when diluted with twice its volume of water); while, when it is boiled in the presence of cotton, the latter takes up 58.7 per cent. of alumina. But in both cases, as mentioned above, the precipitation is completed and the acid neutralized by means of an alkaline bath; thus, with ammonium carbonate:



The following example of a mordanting process is given by Hasluck (*Mordants, Methods, and Machinery used in Dyeing*, p. 13): Prepare a solution of basic aluminium sulphate by dissolving 200 g. of normal aluminium sulphate and 31.82 g. of sodium carbonate in a litre of water. Dilute the solution to a density of  $10^\circ \text{Tw}$ . The cotton is impregnated with this solution, the excess wrung out, and the cotton dried at a low temperature. It is then soaked in a cold bath containing 50 g. of strong ammonia (sp. gr. 0.88) per litre. After working in this bath for from 5 to 10 min., and then washing, it is ready for dyeing. Ammonia may be replaced by sodium phosphate (5 to 10 g. per litre) or sodium silicate (5 to 10 g. of  $100^\circ \text{Tw}$ . solution per litre). The alumina may be fixed also by means of sulphonated oil. The cotton is first impregnated with a solution of Turkey-red oil containing 50 to 150 g. per litre, squeezed, and dried. When dry it is worked in a solution of basic aluminium sulphate of  $10^\circ \text{Tw}$ . density, and then washed.

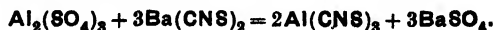
*Aluminium acetates* are used in printing and in Turkey-red dyeing. Normal aluminium acetate may be made either by dissolving the hydroxide in acetic acid or by decomposing aluminium sulphate with lead acetate:



In the latter case the insoluble lead sulphate is removed by filtration or sedimentation. Basic aluminium acetates can be obtained in a similar manner to basic sulphates. Their solutions also become more basic and less soluble when boiled. If sulphates are present, solutions of normal or basic acetates give precipitates when diluted with water, but in the absence of sulphates the basic salts are not precipitated by dilution alone, as are basic sulphates. Moreover, in the presence of sulphates the precipitate formed by boiling a solution of a basic acetate is not redissolved when the solution is cooled. If insufficient lead acetate is used to replace the sulphate completely by acetate groups, salts termed *sulphate-acetates* are obtained, e.g.  $\text{Al}_2(\text{OH})_2(\text{SO}_4)(\text{CH}_3.\text{COO})_2$ . When cotton is impregnated with a solution of a sulphate-acetate and dried, nearly all the contained alumina is deposited. *Red liquor* contains sulphate-acetates. It is made by treating a solution of aluminium sulphate with lead acetate and sodium bicarbonate:

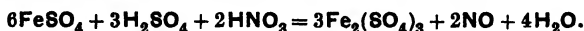


Among other aluminium mordants is the *thiocyanate*, which can be made by treating a solution of aluminium sulphate with one containing barium thiocyanate and filtering off the precipitated barium sulphate:

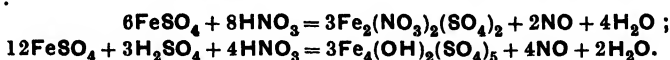


When sodium carbonate is added to a solution of aluminium thiocyanate in limited quantities, basic thiocyanates are produced, such as  $\text{Al}(\text{OH})(\text{CNS})_2$ .

**Mordanting with Iron.**—Ferrous sulphate has already been mentioned, but it is not used much for cotton. Ferric sulphate, under the name of *nitrate of iron*, is more common. A solution of this salt is made by oxidizing ferrous sulphate with nitric acid in the presence of sulphuric acid. This is the origin of the name *nitrate of iron*. The reaction is illustrated by the equation:



Basic ferric sulphates may be prepared in the same way as with aluminium sulphate. By using less sulphuric acid than that required by the equation given above, or by omitting it altogether, salts termed *nitrate-sulphates* are obtained:



Ferric sulphates are used for producing logwood blacks. Cotton is mordanted by soaking in the liquor, squeezing, and then fixing in a cold bath containing sodium carbonate.

*Pyrolignite of iron*, *Ferrous acetate*, is known also as *iron liquor*. It is obtained when pyroligneous acid is treated with iron filings till no more can be dissolved. Commercial iron liquor generally has a specific gravity of 20° Tw. It is used largely for weighting silk, but also to a certain extent for mordanting cotton. The latter is first treated with tannic acid as described under basic dyes, and then passed into a cold solution of pyrolignite of iron.

**Mordanting Silk.**—The mordant dyestuffs are used almost exclusively for wool. Dyed silk is not, as a rule, required to be fast to washing, and brighter colours are produced by the basic and other dyestuffs. But when fastness to washing is required, silk may be mordanted with chromium fluoride or chrome alum. The use of dichromate is inadmissible, as it quickly damages silk. In order to mordant silk it may be steeped in a cold bath of chromium fluoride (2° Tw.) or chrome alum (9° Tw.). After washing, it is then put into a cold solution of sodium silicate of about 1° Tw. strength to precipitate the chromium. It is then washed again, and is ready for dyeing. Mordanted silk is dyed in a bath containing 25 per cent. by volume of boiled-off liquor just "broken" with acetic acid. The dyeing is started in a cold or lukewarm bath, the temperature being raised slowly to the boiling-point, and the bath kept boiling for from one-half to one hour. The goods are then washed, and brightened with dilute acetic acid.

### Dyeing with Mordant Dyestuffs.

In many cases about 4 per cent. of calcium acetate is used as an assistant; it produces brighter colours, probably by forming a double colour lake. Hence hard water does not matter, provided the temporary hardness is just neutralized with acetic acid; it is, in fact, rather an advantage, since it saves the use of calcium acetate. From 2 to 4 per cent. of the dyestuff is used. Soluble dyestuffs are dissolved by making them into a paste with cold water and then adding boiling water with stirring. Pastes are ground to a thin cream with a little dilute acetic acid, and strained into the bath, which contains water previously neutralized with acetic acid. When soft or softened water is used, 4 per cent. of calcium acetate is then added. The goods are wetted down and entered at about 140° F. (60° C.). The temperature of the bath is then raised to the boiling-point, and gentle ebullition maintained for about 30 min.

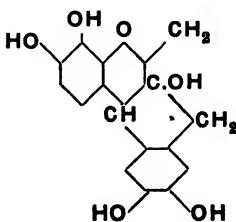


Two per cent. of acetic acid is then added, and the boiling continued for a further 15 min. If it is necessary to add more dyestuff, this should be first mixed with a little acetic acid; the bath is allowed to cool, the goods are lifted, and the dyestuff is added, after which the temperature is raised again to boiling-point. With uneven dyes the dyestuff may be added in portions in the usual manner. An important point in dyeing with mordant dyestuffs is that iron generally affects the colours produced. It has been pointed out that many of these dyes are polygenetic, and they generally give darker shades on iron than on such mordants as alumina.

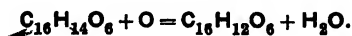
Uneven colours are difficult to correct with mordant dyestuffs. In extreme cases the goods should be partly stripped, and dyed with a darker colour. Sometimes shades can be corrected by means of a neutral-dyeing or weak-acid-dyeing acid dyestuff. It must be remembered that the final colour is determined by the quantity of mordant present and its even distribution.

**Logwood.**—This is one of the few natural dyestuffs which is still extensively used, and, next to indigo, it is the most important. It is used either alone or in conjunction with other dyes, and particularly for wool and silk.

Logwood is extracted from campeachy wood, which is obtained from a tree growing chiefly in South America, though the best variety comes from Honduras and Jamaica. It is sold either as wood, as chips, or in the form of an extract. Freshly cut logwood is colourless, the colouring-matter being present in the form of a glucoside. When moist logwood chips are allowed to ferment, the glucoside is decomposed into glucose and a body termed *hæmatoxylin*. The latter is still colourless. It has the composition  $C_{16}H_{14}O_6 \cdot 3H_2O$ , and is a crystalline substance which is sparingly soluble in cold, though comparatively soluble in hot water. It dissolves freely in alcohol, ether, or carbon disulphide. Hæmatoxylin can be prepared from logwood chips by extracting them in a Soxhlet with ether, and concentrating the ethereal solution in the absence of air. The residue must be kept under water to avoid oxidation. When dissolved in water and recrystallized in the presence of a little sodium bisulphite, colourless crystals are obtained, which have the formula

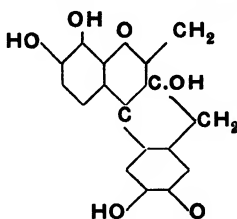


When fused with sodium hydroxide, hæmatoxylin gives pyrogallol,  $C_6H_3(OH)_3$ . Hæmatoxylin has feeble acid properties, forming salts which absorb oxygen when exposed to air, giving rise to *hæmatates*. When hæmatoxylin itself is exposed to air a similar oxidation takes place, *hæmatein* being produced:



Hæmatein may be prepared by passing air through a solution of 15 g. of hæmatoxylin dissolved in 15 ml. of concentrated ammonia and 150 ml. of water for about six hours, and then running the mixture in a thin stream into 250 ml. of 10 per cent. acetic acid heated on the water-bath.

Hæmatein forms reddish-brown crystals with a greenish-yellow metallic lustre, sparingly soluble in hot water, alcohol, and ether. The formula is



Hæmatein is the essential colouring-matter of logwood. It is produced also from hæmatoxylin by the action of oxidizing agents, such as chromium trioxide,  $\text{CrO}_3$ . It has acid properties, combining with metals to form hæmatates.

In dyeing with logwood, either hæmatoxylin or hæmatein may be made use of, but the former must first be oxidized to hæmatein. For this purpose the oxidizing mordant, chromic acid, is employed. The reaction is—



Thus hæmatein and chromium sesquioxide are produced. The hæmatein then combines with the oxide of chromium to form an insoluble colour lake. If only hæmatein is present, no oxidation is necessary, and hence only a basic mordant,  $\text{Cr}_2\text{O}_3$ , is required.

Logwood chips contain both hæmatoxylin and hæmatein, depending upon the degree of oxidation. This can be tested in the following manner: Two skeins of wool are mordanted, one with chromium trioxide,  $\text{CrO}_3$ , and the other with the sesquioxide,  $\text{Cr}_2\text{O}_3$ . These are then dyed under similar conditions in a decoction of logwood chips or a solution of an extract. The skein mordanted with sesquioxide will be dyed only by the hæmatein present in the bath; but the other, mordanted with chromium trioxide, will oxidize any hæmatoxylin present to hæmatein, and this, together with the hæmatein originally present, will be fixed on the wool. If only hæmatein is present, both skeins will be dyed the same colour; but if hæmatoxylin is also present the skein mordanted with chromium trioxide will be dyed deeper than the other. In fact, the proportions of the two substances may be judged from the difference in colour.

When dyeing with logwood, the chips are first boiled with water, and the decoction obtained is used. The chips may be placed in linen bags, and boiled for an hour in the dye-bath. The bags are then lifted, and allowed to drain into the bath. About 3 per cent. of the chips are soluble in boiling water. Extracts are much more convenient to use than chips. These are made by extracting the chips with boiling water, filtering the solution thus obtained, and concentrating it *in vacuo*. Extracts are sold in two forms, viz.: (i) liquid extracts of about 50° Tw. strength, and (ii) crystals. The latter are obtained by oxidizing the extract, and concentrating it till it sets to a crystalline mass on cooling. The crystals consist chiefly of hæmatein, while liquid extracts contain considerable quantities of hæmatoxylin. The proportions depend upon the degree of natural or artificial oxidation. Any proportion of hæmatein may be produced, but, as a general rule, in liquid extracts not more than 20 per cent. of the hæmatoxylin has been oxidized, while in crystalline forms (termed *hæmatein crystals*) from 80 to 95 per cent. of the colouring-matter is present as hæmatein. Liquid extracts are sometimes adulterated with extracts of other

woods, such as chestnut, or with molasses and other substances. Thus the specific gravity of an extract is not necessarily a criterion of its dyeing value. Extracts should be tested by the sample dyeings described above.

Logwood is a typical polygenetic dyestuff, giving the following colours with different common mordants:—

Iron . . . . .	Grey to black
Copper. . . . .	Greenish-blue to black
Chromium . . . . .	Blue to black
Aluminium . . . . .	Violet
Tin . . . . .	Purple

Its chief application is in dyeing blacks. Logwood blacks are fast, but have one disadvantage: they are liable to become green when exposed to light. This is generally inhibited by the addition of a red or violet coal-tar dyestuff.

*Detection.*—A solution containing hæmatein and hæmatoxylin (*i.e.* logwood extract or decoction) gives the following reactions: (i) a black precipitate when boiled with potassium dichromate; (ii) a red colour with mineral acids; (iii) a bluish-black precipitate with basic lead acetate; (iv) a reddish-violet precipitate with stannous chloride; (v) a violet colour with alum; and (vi) a purple colour, subsequently changing to brown, with caustic alkalis.

If a fabric dyed with logwood is boiled with dilute (5 per cent.) hydrochloric acid, most of the colour is extracted, giving a red solution, which becomes violet when neutralized with lime-water. When treated with 10 per cent. sodium hydroxide solution, the colour of the fabric is changed to violet. The detection of the mordant is important, since its absence is incompatible with the presence of any mordant dyestuff.

**Logwood Black on Wool.**—This is an important colour, either alone or in combination with others. Logwood black is nearly always dyed on a chrome mordant, the acid oxide,  $\text{CrO}_3$ , being used. The wool is mordanted with 3 per cent. of potassium dichromate and 1 per cent. of sulphuric acid, as described above. The mordanted wool may then be dyed with from 10 to 15 per cent. of logwood extract for from one to one and a half hours at the boiling-point. Calcium acetate is not used with wool which has been mordanted with potassium dichromate and sulphuric acid. When fully oxidized logwood extracts (or hæmatein crystals) are used, logwood blacks may be dyed on basic chromium sesquioxide, obtained with potassium dichromate and cream of tartar.

This process gives a blue-black. This blue tint may be changed to a *dead* black by adding 5 per cent. of fustic to the dye-bath. If less than 15 per cent. of logwood is used, the shade is bluer. With from 1 to 5 per cent. it is entirely blue. If the proportion of fustic is increased, the shade becomes greenish. Instead of using fustic for shading, about 0.25 of Alizarine Yellow may be employed.

The addition of a little copper sulphate to the mordanting bath improves the colour, the copper acting probably as an oxygen-carrier in the dye-bath. From 1 to 2 per cent. of crystalline copper sulphate may be used with the usual quantities of potassium dichromate and sulphuric acid. Either copper sulphate or acetate is sometimes added to the dye-bath for the same purpose when oxidized extracts are employed.

The shade may be changed to violet-black by the addition of stannous chloride to the dye-bath. The goods are dyed with logwood extract till the bath is nearly exhausted. About 2 per cent. of stannous chloride previously dissolved in water is then added, and the dyeing continued for 15 min. at the boiling-point.

Logwood blacks are commonly after-treated to improve their fastness and to fix any loosely combined dyestuff, which might subsequently rub off. This consists in *back-chroming*. After rinsing the dyed goods, they are worked at 180° F. (82.2° C.) in a bath containing 1 per cent. of potassium dichromate. Ferrous sulphate is also used: the goods after dyeing and rinsing are treated in a warm bath containing 3 per cent. of the salt. This method tends to produce a dead black, or to *sadden* the colour. The ferrous sulphate is sometimes added to the dye-bath for the same purpose. While back-chroming is advantageous, over-chroming when mordanting is, on the contrary, harmful, particularly when potassium dichromate and sulphuric acid are used. It oxidizes the wool fibre, causes the dye to be unevenly absorbed, and tends also to produce grey shades. Uneven shades may be caused also by exposing the mordanted goods to air or light before dyeing. Back-chromed goods must be very thoroughly washed, since unremoved potassium dichromate subsequently affects the colour, causing it to become greenish.

All logwood blacks are liable to become greenish when exposed to light for a long time. This tendency can be corrected by adding a little red colour to the dye-bath. An alizarine red may be used. Logwood-black dyed on an iron mordant is less liable to become green than when dyed on chromium; hence, also, after-treatment with ferrous sulphate has a similar effect. In order to obtain an iron black, either a single- or double-bath process may be used. For the latter, the goods are mordanted by dissolving separately (a) from 3 to 6 per cent. of ferrous sulphate, 2 per cent. of copper sulphate, and 2 per cent. of alum; and (b) 8 to 12 per cent. of cream of tartar. The two solutions are mixed, and the goods are wetted down, entered at about 140° F. (60° C.), and then boiled gently for an hour in the bath. The copper sulphate is necessary as an oxygen-carrier. The mordanted goods are then dyed in the usual way with logwood and fustic. In this case calcium acetate (4 per cent.) is added to the dye-bath when soft water is used. With hard water the temporary hardness must be neutralized with acetic acid.

For a single-bath process the following may be used: The goods are boiled with from 10 to 15 per cent. of logwood extract and 5 per cent. of fustic for an hour. They are then lifted, and the bath is allowed to cool. A solution of 4 to 6 per cent. of ferrous sulphate and 2 per cent. of copper sulphate is next added, and the goods are returned to the bath. The temperature is then raised to 100° F. (37.8° C.) for three-quarters of an hour, and finally to the boiling-point for half an hour.

*Bonsor's Black.*—The insoluble logwood-chromium lake is prepared by boiling logwood extract with potassium dichromate. This is separated, and mixed with ferrous sulphate and copper sulphate to form a paste. Although insoluble in water, it dissolves in oxalic acid. Wool is dyed directly with the paste. About 25 per cent., together with from 2 to 3 per cent. of oxalic acid, is used. The goods are dyed at the boiling-point, a little sodium carbonate being added towards the end of the operation, if necessary, to neutralize some of the acid and to assist exhaustion. Acid dyestuffs may be added to the bath if desired. A direct logwood-black solution may be prepared quite simply by boiling a solution of logwood extract with a little potassium dichromate, collecting the precipitated colour lake, and dissolving it in dilute oxalic acid.

Gardner's single-bath process may be noted also. The bath is made up with from 6 to 8 per cent. of chrome alum, 3 to 4 per cent. of oxalic acid, 1 per cent. of ground chalk, and 25 per cent. of logwood extract. Dyeing is carried out at the boiling-point, sodium carbonate being used if necessary.

*Woaded Blacks.*—Wool is sometimes dyed first with indigo and then with

logwood black to produce woaded blacks. The goods are dyed to a medium shade with indigo in the ordinary manner. They are then mordanted with about 2 per cent. of potassium dichromate or of ferrous sulphate and 4 per cent. of cream of tartar. No sulphuric acid must be used, since dichromate and sulphuric acid would oxidize the indigo. After mordanting, the goods are washed, and dyed with about 10 per cent. of logwood extract and from 2 to 5 per cent. of fustic. The indigo can be detected and estimated by the methods described later.

*Logwood Blues.*—It has been noted that when light shades of logwood are dyed on a chrome mordant a blue colour is produced. These blues are used alone, or in conjunction with indigo to cheapen the process. For the latter, the goods are dyed first with indigo as for woaded blacks, then mordanted lightly with potassium dichromate, and dyed with logwood extract. Alternatively an aluminium mordant may be employed. A purple tint may be obtained by adding from 0.5 to 1 per cent. of stannous chloride to the dye-bath towards the end of the process.

Pure logwood blues are dyed by the two-bath process on an aluminium mordant. The goods are first mordanted with from 4 to 6 per cent. of aluminium sulphate, or 6 per cent. of alum and 6 per cent. of cream of tartar, and well washed. They are then dyed with 10 per cent. of logwood extract, 4 per cent. of calcium acetate being used as an assistant. The shade of blue produced depends upon the amount of mordant used. Increasing the quantity of mordant gives a reddish shade, while the addition of stannous chloride to the dye-bath gives an indigo-like effect.

*Logwood purple* may be dyed by mordanting the wool with 4 per cent. of stannous chloride and 4 per cent. of oxalic acid as described above, and then dyeing with 10 to 15 per cent. of logwood extract, but without the addition of calcium acetate.

*Logwood on Cotton.*—Logwood is not used very extensively for cotton, since direct and sulphur blacks are much simpler to employ owing to the lack of affinity of cotton for mordants, but it is often used in connection with these for topping.

Logwood black is dyed on cotton on an iron mordant fixed by tannic acid. Either nitrate or pyrolignite of iron may be used, while sumac or myrobalans are generally employed as the source of tannic acid. But the iron may be fixed also, if preferred, by either sodium carbonate or milk of lime. The following are examples of the methods:—

(1) The cotton is soaked in a cold bath of either nitrate or pyrolignite of iron of about 4° to 5° Tw. strength. It is then squeezed, and worked in a cold solution of sodium carbonate (5° Tw.) or milk of lime, and finally washed thoroughly with water. It is then dyed in a separate bath with about 15 per cent. of logwood extract and 5 per cent. of fustic. Logwood black is inclined to have a rusty appearance. The addition of a little copper sulphate (1 to 2 per cent.) to the dye-bath tends to correct this. Further improvement is effected by after-chroming, by working the dyed goods at 180° F. (82.2° C.) in a bath containing from 0.5 to 1 per cent. of potassium dichromate. Another method of after-treatment is to add 1 to 2 per cent. of ferrous sulphate to the dye-bath, put the goods back, and heat the bath to the boiling-point for half an hour. After this, the cotton is treated in the usual manner for blacks by working it in a bath of soap and olive oil. This both improves the colour and gives the goods a softer feel.

(2) The previous method is comparatively cheap, but better results are obtained if the iron is fixed with tannic acid. The cotton is wetted down in

a bath containing sumac extract or decoction of 4° Tw. strength. The temperature is brought to the boiling-point, and the bath is then allowed to cool in order that the cotton may take up the maximum quantity of tannic acid. It is then squeezed, and soaked in a cold bath of nitrate or pyrolignite of iron of 4° Tw. for half an hour. At the end of this time it is removed, squeezed, treated with lime-water, and then finally washed. The dyeing and after-treatment are the same as before.

There are many varieties of *single-bath* methods. Hummel's process is as follows: The goods are wetted with boiling water, and then boiled in a bath containing about 30 per cent. of logwood extract. They are then drained and exposed to air for some time, after which oxidation is completed by working in a cold solution containing 8 per cent. of potassium dichromate and 6 per cent. of copper sulphate. The goods are then washed, and dyed again in a bath containing 10 per cent. of logwood extract, starting cold and raising the temperature gradually to the boiling-point. They are then washed, soaped, and dried. The following method is rather simpler: A solution of 1.5 per cent. of potassium dichromate, 3.5 per cent. of hydrochloric acid, and 15 per cent. of logwood extract is prepared. The cotton is worked for some time in this at ordinary temperatures, and then raised gradually to the boiling-point. Or the logwood may be added to the bath in portions during the operation. By this method a bluish-black is obtained, which, however, becomes black by the addition of fustic to the bath or by after-treatment with ferrous sulphate.

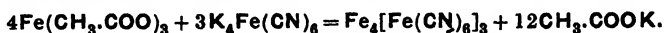
Zänker (*J. Soc. Chem. Ind.*, 1907, 26, 317) uses ferric ammonium oxalate, either alone or with copper sulphate, either in a neutral or in an acid dye-bath. The dyed material is after-treated with potassium dichromate.

*Logwood greys* may be obtained by dyeing in a bath containing 5 per cent. of logwood extract and 1 per cent. of ferrous sulphate. But better results are produced if a two-bath method is used. For this the cotton is first worked in the logwood solution, and then transferred to the ferrous-sulphate bath.

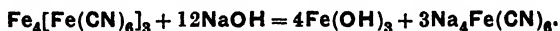
**Logwood on Silk.**—One of the chief applications of logwood is in dyeing weighted black silk on an iron mordant. The weighting and dyeing are combined, giving a full black, opaque fibre. But logwood is used also for silk without weighting, the colour being termed a *pure black*. The principles of silk-weighting have been described briefly in Chapter XIII. Logwood black is dyed on both raw and boiled-off silk. Heavily weighted silks are weighted and dyed in the gum, chestnut extract and pyrolignite of iron being commonly used, since these give a bluish-black colour to the weighted goods, which cannot be obtained otherwise. Hummel gives the following method of application:—

The silk is soaked for some hours at 40° to 45° C. in a solution of chestnut extract containing 100 per cent. of tannic acid (or from 10° to 15° Tw.). It is then squeezed, and put into a cold bath of pyrolignite of iron of from 12° to 14° Tw. This converts the tannic acid into ferrous tannate. After about an hour the goods are squeezed, exposed to air to oxidize the ferrous to ferric iron, and then washed. This treatment adds from 20 to 30 per cent. to the weight. If more weight is required, the process is repeated. By means of fifteen repetitions an increase of 400 per cent. can be obtained. The mordanting baths are maintained at the necessary strength by fresh additions of pyrolignite and chestnut. The acidity of the iron bath is occasionally corrected by the addition of iron turnings, followed by heating of the bath nearly to the boiling-point. A bath of potassium ferrocyanide may be made use of at the

end of the weighting process; it adds weight and gives a bluish tone owing to the formation of Prussian blue:



After weighting, the silk is dyed with 10 to 15 per cent. of logwood extract, 5 per cent. of fustic, and 4 per cent. of calcium acetate. After dyeing, it is exposed to air for some time, and then treated with soap and olive-oil emulsion in the usual manner for blacks. When Prussian blue is used, it must be remembered that it is decomposed by alkalis with the formation of ferric hydroxide and sodium ferrocyanide:



Pyrolignite may be replaced by nitrate of iron, i.e. basic ferric sulphate, for boiled-off silks. *Lyons Black* is an example. The silk is first soaked in a cold bath of nitrate of iron of 10° to 15° Tw. for an hour. It is then wrung, and worked in a cold bath containing sodium carbonate or other mild alkali (3° to 5° Tw.). Finally it is treated with potassium ferrocyanide and hydrochloric acid. These operations are repeated if necessary, till the weighting is sufficient. The weighted silk is then dyed with logwood, fustic extract, and calcium acetate as above.

**Weighting of Silk in Logwood Dyeing.**—Hummel gives the following description of the application of *Lyons Black* for dyeing boiled-off silk and bringing it to its original weight or weighting it moderately:

The silk is first soaked in a cold bath of basic ferric sulphate of 50° Tw. strength, and washed. After washing, it is soaped carefully at about 85° to 90° C. It is then dyed blue with 20 per cent. of potassium ferrocyanide and an equal weight of hydrochloric acid (30° Tw.), the latter being added in two portions. Next, it is again mordanted with basic ferric sulphate, washed, and soaked in a bath containing 50 to 100 per cent. of catechu at 60° to 80° C. After this it is mordanted by soaking in a cold solution of aluminium sulphate to give a violet or blue-black shade when dyed. After washing again, it is dyed with logwood, with a little fustic if the shade is too violet.

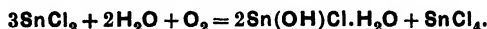
When it is desired only to make good the loss caused by boiling-off, the silk may be simply weighted with tannic acid after dyeing. It is rinsed, and entered into a boiling bath of sumac extract at about 2° Tw. strength. After turning the silk a few times, the bath is allowed to cool to 100° F. (37.8° C.), when the silk is removed, rinsed, and brightened with acetic acid. It is generally necessary to add a little dye to the tannic-acid bath to bring the colour up to the necessary shade. The dyeing and weighting may be combined by dyeing the silk as nearly as possible to shade in a bath of broken boiled-off liquor, and then adding carefully the sumac extract. A slight amount of weighting may also be added, working the dyed silk in a solution of sugar of about 5° Tw. strength. *Compounds of tin* are used also for imparting a moderate amount of weighting to silk, the chief being (i) oxide, (ii) phosphate, and (iii) silicate. These processes depend upon the fact that silk is able to adsorb stannous and stannic chloride from their aqueous solutions. The adsorbed tin salt is then partly decomposed by hydrolysis, and the change completed by double decomposition (see below).

*Stannous Chloride* is a white crystalline substance with the composition  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . It is produced by dissolving granulated tin in hydrochloric acid, concentrating the solution, and allowing it to crystallize. The crystals obtained are known also as *tin crystals*, or *tin salt*. Sometimes the solution is only partly concentrated, the strong solution thus obtained being termed

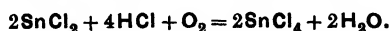
*muriate of tin.* When stannous chloride is dissolved in a small quantity of water, a clear solution is obtained, but if the solution is diluted a basic salt is precipitated:



This basic salt redissolves on adding more hydrochloric acid. When exposed to air, solutions of stannous chloride absorb oxygen, giving the insoluble basic chloride and soluble stannic chloride:

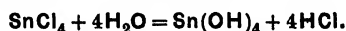


This oxidation takes place also in the presence of excess of hydrochloric acid, but in this case the formation of the basic chloride is prevented:



This explains why stannous chloride in the presence of hydrochloric acid acts as a powerful reducing agent, and its use in testing for sulphur dyestuffs. Stannous chloride is used in mordanting wool for certain colours, such as Cochineal Scarlet. It is also added in certain cases to a dye-bath to brighten the shade. It is employed also in cotton-printing and for weighting silk in connection with catechu.

*Stannic Chloride*,  $\text{SnCl}_4$ , is obtained when excess of chlorine is passed over granulated tin, or when a stream of the gas is led into a solution of stannous chloride. It forms a colourless fuming liquid boiling at  $114^\circ \text{C}$ . With a small quantity of water it forms a crystalline hydrate,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ . When this is dissolved in excess of water, it undergoes hydrolysis slowly, with the formation of stannic hydroxide:

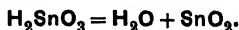


At ordinary temperatures this decomposition takes place only slowly, but if the solution is boiled the salt is completely decomposed. When a solution of stannic chloride is mixed with one containing ammonium chloride, and the mixture concentrated, crystals of the composition  $\text{SnCl}_4 \cdot 2\text{NH}_4\text{Cl}$  are obtained. These constitute the *pink salt* of commerce. This compound dissolves in water without change, but when its solution is boiled, it is hydrolysed as is stannic chloride.

When solutions of stannic chloride are diluted, it is probable that the first product is soluble stannic acid,  $\text{Sn(OH)}_4$ . Boiling converts this into insoluble metastannic acid:



Metastannic acid when dried gives up water, forming stannic oxide,  $\text{SnO}_2$ :



Stannic chloride is the chief starting-point for the weighting of silk with tin. Obviously the simplest process would be to soak the silk in a solution of stannic chloride, and then precipitate the insoluble stannic hydroxide by diluting or washing with hot water. This method, however, is capable of giving only a small amount of weighting, and, as a rule, the tin is fixed by means of either sodium carbonate, phosphate, or silicate. The following are examples:—

(1) *Tin Oxide*.—The silk is soaked for an hour in a cold bath of stannic chloride of  $53^\circ \text{Tw}$ . density. It is then washed with water and hydro-extracted. Silk adsorbs considerable quantities of stannic chloride from its solutions. When washed with water this becomes partly hydrolysed, causing the precipitation of stannic hydroxide on the fibre. Ley (*J. Soc. Chem. Ind.*, 1913, 32, 81) suggests that the preliminary adsorption is followed by a chemical change

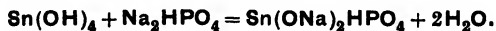


within the fibre, resulting in the formation of stannic hydroxide, which then combines with more stannic chloride to form an insoluble oxychloride.

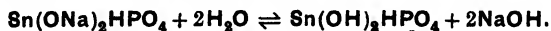
This is stated somewhat differently by Fichter and Müller (*J. Soc. Chem. Ind.*, 1914, 33, 689), whose theory is that first an addition product is formed between the amino-acid fibroin of the silk and the stannic chloride. They have isolated such addition products in the case of such analogous substances as glycocoll, which have the constitution  $\text{Sn}(\text{amino acid})_4\text{Cl}_4$ . These bodies are soluble in water and undergo progressive hydrolysis, the amino acid and chlorine being gradually replaced by hydroxyl, until finally stannic oxide is left. Similar addition products are probably formed in silk-weighting, hydrolysis taking place in the washing. At the end of the process the fibroin is restored to its original condition, and is ready to take up a fresh charge.

After hydro-extraction the silk is soaked in a lukewarm bath of sodium carbonate or other alkali of about 2° Tw. strength. This completes the precipitation of the tin as hydrated stannic oxide. The silk is then washed again. This treatment adds about 10 per cent. to its weight. By several repetitions a maximum of 50 per cent. can be reached. After weighting, the silk is worked for half an hour in a hot soap-bath containing 30 per cent. of soap, and is finally washed, and brightened with a little acetic acid.

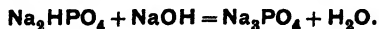
(2) *Tin Phosphate*.—The silk is soaked as before in stannic chloride solution, but sodium phosphate solution (7° to 8° Tw.) is used instead of sodium carbonate. For souple silk the temperature of this bath is 120° to 140° F. (48.9°–60° C.), for boiled-off silk 160° F. (71.1° C.). After treatment the silk is washed as before. This adds about 20 per cent. to the weight, which can be increased to 100 per cent. by repetition. The reactions which take place in this process are not clearly understood. Ley (*loc. cit.*) thinks that the stannic oxide produced by hydrolysis of the stannic chloride is first converted into sodium stannate, which reacts with free phosphoric acid to form a tin phosphate of the formula  $\text{SnO}_2 \cdot \text{P}_2\text{O}_5$ ,  $2\text{SnO}_2 \cdot \text{P}_2\text{O}_5$ , or  $3\text{SnO}_2 \cdot \text{P}_2\text{O}_5$ . Heermann (*J. Soc. Chem. Ind.*, 1914, 33, 72) holds a different view. According to this, stannic hydroxide reacts with the sodium phosphate in accordance with the equation:



The double salt is stable only in the presence of sodium phosphate. On washing with water it is hydrolysed, thus:



The free alkali is then neutralized by the excess of sodium phosphate in the wash water:



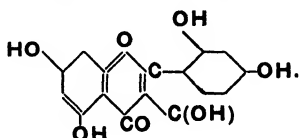
(3) *Tin Silicate*.—In this case a warm bath of sodium silicate (5° Tw.) is used to fix the tin chloride. The silk is worked in this for half an hour at a temperature of 160° F. (71.1° C.), and then washed as before, and brightened.

When a tin salt is employed for weighting silk (F. Müller, *J. Soc. Chem. Ind.*, 1909, 28, 471), the weighting cannot be carried beyond a certain point without risk of damage to the fibre, the damage becoming evident during dyeing and finishing, on storing, or in wear. But if aluminium chloride is used, either alone or with stannic chloride, there is less risk of damage. The handle is improved by a treatment with cerium chloride. The process consists of a treatment with a solution of aluminium chloride of 52° Tw., followed by a bath of sodium phosphate and rinsing. The operations are repeated till the desired weighting is obtained.

Logwood black cannot be dyed on a tin mordant alone. After weighting, the silk must be soaked in a solution of ferrous acetate or basic ferric sulphate, and the iron fixed by means of tannic acid in the manner already described. But stannous chloride is used directly in dyeing black silk because it assists in fixing tannic acid (as tannate of tin), and also because it gives a bluish or violet tone to the logwood. Thus, for a weighted black of this type the following example is given by Hummel: (i) mordant with basic ferric acetate and then soap, repeating the operations from one to eight times according to the amount of weighting required; (ii) dye blue with potassium ferrocyanide and hydrochloric acid; (iii) soak in a bath containing 100 to 150 per cent. of catechu and 10 to 15 per cent. of stannous chloride at 60° to 80° C.; then soak in a fresh bath containing 100 to 200 per cent. of catechu; (iv) mordant with ferrous acetate; and (v) wash and dye with logwood extract.

Silk weighted with tin is liable to develop stains and tenderness. The causes of this have been referred to in Chapter XIII, and also the analysis of weighted silk.

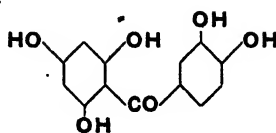
**Fustic** is a natural dyestuff obtained from the wood of the trunk of *Chlorophora tinctoria* and *Maclura tinctoria*, and exported from Central and South America, Cuba, and Jamaica. The best quality is Cuban *old fustic*. The dyestuff is sometimes termed *old fustic* to distinguish it from *young fustic*. It is used in the form of either chips or extract. It contains two colouring-matters, the more important being morin,  $C_{15}H_{10}O_7$ , or



*Morin* can be prepared from fustic chips in the following manner (*Society of Dyers and Colourists' Colour Index*, p. 292): A little acetic acid is added to a boiling extract of the rasped wood of old fustic, followed by a solution of lead acetate. A yellow lead compound of morin is precipitated, which is filtered off and washed. The washed precipitate is made into a thin paste with water, and this is poured into boiling dilute sulphuric acid. The lead sulphate is filtered off, and the filtrate cooled. Crude morin crystallizes out. This is recrystallized from alcohol. The crystals contain traces of another body termed *maclurin*. This can be removed entirely by dissolving the morin in glacial acetic acid and adding a little hydrochloric acid, when morin hydrochloride is precipitated. Pure morin is a colourless crystalline substance, forming glistening needles with a bitter taste and melting at 285° C. It is sparingly soluble in water, but moderately soluble in alcohol. It gives a yellow solution with sodium hydroxide, which turns brown on exposure to air. Its solutions give a bright orange precipitate with lead acetate, and an olive-green colour with ferric chloride. Morin is a polygenetic mordant dyestuff, giving the following colours:—

Mordant.	Colour.
Chromium . . . .	Olive-yellow
Aluminium . . . .	Yellow
Tin . . . . .	Lemon-yellow
Iron . . . . .	Deep olive-brown
Copper . . . . .	Olive

*Maclurin*,  $C_{13}H_{10}O_6$ , or

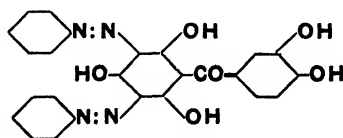


the second colouring-matter, is prepared by removing the lead from the filtrate from the lead compound of morin (obtained as above), concentrating the filtrate, and extracting with ethyl acetate. It forms colourless prismatic crystals with a sweet taste and melting at  $200^{\circ}$  C. It is somewhat more soluble in water than morin, and gives the following reactions: (i) a pale yellow solution with sodium hydroxide; (ii) a yellow precipitate with lead acetate, soluble in acetic acid; (iii) a greenish-black colour with ferric chloride; and (iv) a precipitate with tannic acid. *Maclurin* dyes wool as follows:—

Mordant.	Colour.
Aluminium . . .	Pale yellow
Chromium . . .	Yellowish-green
Iron . . .	Weak grey

*Fustic* is used alone for dyeing wool to a certain extent. When dyed on a chromium mordant it gives a good yellow (varying from olive-yellow to old gold), which is fast to light. An orange-yellow is also obtained on wool by a single-bath process, using 4 per cent. of stannous chloride, 4 per cent. of oxalic acid, and 50 per cent. of *fustic*. With wool mordanted with copper and iron, greenish-olive colours are produced, fast to light, washing, and milling. Yellow shades produced with tin and aluminium are not very fast to light. The chief use of *fustic* is for dyeing wool mordanted with chromium in conjunction with logwood and alizarine for olive, brown, and drab as a bottom for black, and also for shading blacks.

*Fustic* extracts are made in the same way as logwood extracts, and commonly have a density of  $50^{\circ}$  Tw. Calico Yellow (Gy.) is a bisulphite compound of *fustic* extract, *i.e.*  $C_{15}H_{10}O_7 \cdot NaHSO_3$ . Patent Fustin or Wool Yellow is made by adding a solution of diazotized aniline hydrochloride to one containing *fustic* extract. It is a yellowish-brown powder, which dyes wool, either mordanted or unmordanted, from an acid bath, giving brownish-yellow colours moderately fast to light and milling, and of good fastness to stoving. It is chiefly bis-benzenediazo-*maclurin*,



**Dyeing with *Fustic*.**—As mentioned above, *fustic* is used chiefly in connection with logwood and alizarine for shading purposes. But wool dyed with *fustic* alone on a chromium mordant is a good yellow, fast to light, soaping, and milling. The wool is mordanted by boiling it for from one to two hours with 3 per cent. of potassium dichromate and dyeing with 50 per cent. of *fustic*. The use of acid or cream of tartar when mordanting is not to be recommended. Brighter shades can be obtained by mordanting with aluminium, and particularly with tin, but the colours are not fast to light. Single-bath methods give the brightest shades. The following formulæ may be used:—

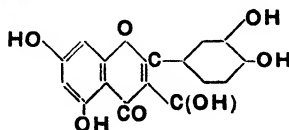
(1) The wool is dyed for an hour at the boiling-point in a bath containing 4 per cent. of aluminium sulphate, 2 per cent. of oxalic acid, and from 25 to 50 per cent. of fustic. The addition of 2 per cent. of stannous chloride gives a much brighter shade. The wool may be mordanted first, if desired, by boiling it with about 8 per cent. of aluminium sulphate.

(2) Use 4 per cent. of stannous chloride, 4 per cent. of oxalic acid, and 50 per cent. of fustic, and dye at the boiling-point; or mordant the wool first with 8 per cent. of stannous chloride and 8 per cent. of potassium hydrogen tartrate.

**Quercitrin Bark.**—This is the ground inner bark of a species of oak growing in North America. It is sold also as a liquid extract (or *bark liquor*), and in the solid form as *flavine*; the latter occurs in two forms, namely the yellow shade and the red shade. The colouring-matter of quercitrin is a glucoside known as *quercitrin*,  $C_{21}H_{20}O_{11} \cdot 2H_2O$ . This may be prepared from the bark by extracting it thoroughly with five to six times its weight of 50 per cent. alcohol, concentrating the solution to half its volume, and adding a little acetic acid and lead acetate solution. This precipitates the dissolved impurities, which are removed by filtration. A stream of sulphuretted hydrogen is then passed through the filtrate to precipitate the excess of lead as sulphide. This is filtered off, and the filtrate is evaporated to dryness. The residue is dissolved in alcohol, and precipitated by the addition of water. If it is dissolved in dilute alcohol and allowed to crystallize, nearly pure quercitrin is obtained. It forms pale yellow crystals melting at  $183^\circ$  to  $185^\circ$  C., or when anhydrous at  $250^\circ$  to  $252^\circ$  C.

Quercitrin dyes wool the following colours: golden-yellow on aluminium, brownish-yellow on chromium, lemon-yellow on tin, and olive on iron. The colours produced by the bark itself are somewhat different, being yellow on aluminium, olive-yellow on chromium, orange on tin, and greenish-olive on iron. They have good fastness to soaping and milling, but are only moderately fast to light (*Society of Dyers and Colourists' Colour Index*, p. 293).

When quercitrin is boiled for some hours with dilute sulphuric acid, it is decomposed into a sugar, rhamnose, and quercetin, which forms pale yellow needles, of the formula  $C_{15}H_{10}O_7$ , or



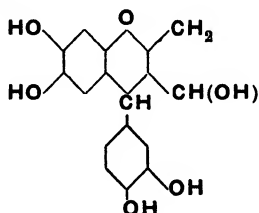
*Quercetin* is comparatively soluble in boiling, but only sparingly soluble in cold, water. It dissolves in alkalis, giving a yellow solution which turns brown on exposure to air. When its solution is treated with lead acetate, an orange-red precipitate is produced, and with ferric chloride a dark green-coloured solution. It dyes wool brownish-orange on aluminium, reddish-brown on chromium, bright orange on tin, and olive-black on iron. Quercetin is the chief constituent of *flavine* (yellow shade).

*Flavine* is an olive-yellow to dark-brown powder of about sixteen times the strength of quercitrin. It is used for dyeing wool by itself, and also for shading logwood blacks in the same way as fustic. It is generally used in place of the bark. Single-bath methods are applicable for dyeing with *flavine* alone. For *Flavine Yellow* the wool may be boiled for from 30 to 45 min. with from 4 to 8 per cent. of stannous chloride, with or without 4 per cent. of cream of tartar or oxalic acid. It is then lifted, from 1 to 8 per cent. of *flavine* added, and the

bath boiled for from 5 to 10 min. The wool is then returned, and the bath boiled again for half an hour. The shade obtained varies from canary-yellow with 1 per cent. of dyestuff to orange with 8 per cent. Flavine and cochineal are used together for producing scarlet and orange on wool. These are dyed by a single-bath process on a tin mordant in the presence of oxalic acid. Thus, the bath may contain from 5 to 8 per cent. of stannous chloride, the same quantity of oxalic acid, and 20 per cent. of cochineal, with sufficient flavine to produce the required shade. The goods are introduced, after wetting down, into the cold bath, the temperature is raised gradually to the boiling-point, and dyeing continued at this temperature for an hour.

**Cutch, catechu**, is an extract made from the wood and fruit of acacia and mimosa trees. *Gambier catechu* is made from the leaves and twigs of a bush, *Uncaria gambir*; mangrove cutch is extracted from the bark of the mangrove tree. Patent or prepared cutch is made by melting gambier catechu with about 1 per cent. of potassium dichromate, with or without a little copper sulphate, and again solidifying the mixture. The extracts are made by extracting the raw material with boiling water, and concentrating the solution till it sets on cooling. Catechu contains two colouring-matters, catechin and catechutannic acid.

*Catechin*,  $C_{15}H_{14}O_6 \cdot 4H_2O$ , or



can be prepared by extracting powdered cutch with boiling ethyl acetate, evaporating the solution, dissolving the residue in ten times its weight of boiling water, and allowing it to crystallize. The crude product is dissolved again in boiling water, and lead acetate solution added as long as a coloured precipitate is formed. The latter is filtered off, and the filtrate treated with sulphuretted hydrogen to remove the lead. After filtering off the lead sulphide, the filtrate is allowed to crystallize.

Catechin forms colourless needle-shaped crystals, very sparingly soluble in cold, but readily soluble in boiling water. The crystals melt at  $96^{\circ}C$ ., but if the water of crystallization is removed, at  $176^{\circ}$  to  $177^{\circ}C$ . Its solutions give a colourless precipitate with lead acetate, and a green colour with ferric chloride.

Catechin dissolves in solutions of alkalis. These solutions absorb oxygen when exposed to air, giving a black precipitate termed *japonic acid*. The same product is obtained when a solution of catechin or catechu is heated with potassium dichromate, especially in the presence of copper sulphate. This precipitate is the colour lake.

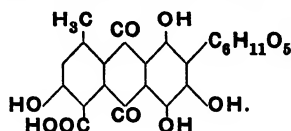
**Catechutannic Acid.**—When catechu is boiled with water, both the catechin and the catechutannic acid dissolve. But when the solution is cooled, the former crystallizes out, leaving the latter in solution. If the solution is evaporated, the catechutannic acid is obtained. It can be purified by dissolving it in alcohol, precipitating the impurities with ether, filtering, and evaporating the filtrate. Catechutannic acid is a reddish-brown powder, which gives the reactions of pyrogallol tannins. Thus it precipitates gelatin

from its solutions, and gives a bluish-black colour with iron salts. It is soluble in alkalis, the solution becoming red on exposure to air.

Catechu is used as a mordant in dyeing cotton with basic dyes; good samples contain 60 per cent. of tannic acid. It is used also for dyeing cotton, and in the dyeing and weighting of silk. It finds employment also in shading or producing compound shades with logwood, fustic, and alizarine. Cotton is dyed brown by boiling it with cutch, and then, after squeezing, treating it in a bath at 140° F. (60° C.) with 2 per cent. of potassium dichromate to oxidize the catechu to japonic acid. If copper sulphate is added to the first bath, deeper shades are produced. Instead of after-treating with potassium dichromate, basic dyestuffs may be used, since the catechutannic acid acts as a mordant for these colours. Wool can be dyed in the same way as cotton, either as above, or together with other mordant dyes such as logwood.

Silk can be dyed black and heavily weighted by means of catechu. The following process is taken from Hummel (*Dyeing of Textile Fibres*, p. 371): The boiled-off silk is steeped in a solution of basic ferric sulphate and then in potassium ferrocyanide to produce Prussian blue. It is then worked at 60° to 70° C. in a bath containing 100 to 200 per cent. of catechu. If only little weighting is required, the catechu bath should have a strength of 4° to 5° Tw., its temperature not exceeding 50° C.; at this temperature only the silk takes up the tannic acid. But at 70° C. the Prussian blue also is acted on; a portion of the tannin is destroyed, but the remainder combines with the iron oxide, giving an increase of weight of from 30 to 40 per cent. For maximum weighting, stannous chloride is used with the catechu. The silk is first worked in a catechu bath for an hour at 50° C. It is then lifted, and 5 to 15 per cent. of stannous chloride is added to the bath. After this has dissolved, the silk is returned, and worked for from one to two hours at 70° to 75° C. The stannous chloride acts as a reducing agent, facilitating the formation of ferroso-ferric oxide; and at the same time stannic hydroxide is formed and fixed on the silk. After weighting, the silk is dyed with logwood in the usual manner.

**Cochineal** consists of the dried powdered bodies of the female of a species of beetle, *Coccus cacti*, which lives on plants belonging to the prickly-pear family growing in Mexico, Central and South America, and the East and West Indies. The colouring principle is known as *carminic acid*,  $C_{22}H_{20}O_{13}$ , or



Carminic acid may be prepared (*Society of Dyers and Colourists' Colour Index*, p. 295) by mixing a solution of the ground beetles in five times their weight of water, with four times its volume of glacial acetic acid, filtering, and keeping over sulphuric acid. It crystallizes in red prisms, which, when heated, darken at 130° C., and become black at 250° C. Carminic acid dissolves in water, giving a scarlet-red solution, which becomes violet with alkalis. Cochineal is a polygenetic dyestuff, giving the following colours: purple on chromium, crimson on aluminium, scarlet on tin, and purple on iron. It is used chiefly for dyeing wool and silk scarlet or red; for example, for hunting-coats, since it is more brilliant and faster to light than acid scarlets.

Wool is mordanted with 6 per cent. of stannous chloride and 6 per cent. of

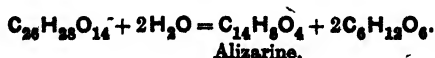
oxalic acid, and then dyed with 20 per cent. of cochineal. Or it may be dyed by a single-bath process by dissolving the dyestuff and oxalic acid in the bath and then adding the stannous chloride. The addition of some yellow dyestuff, such as fustic, improves the colour. Cream of tartar is also used instead of oxalic acid when the wool is mordanted first. The use of an acid solution of stannous chloride in the single-bath process has advantages. The presence of free hydrochloric acid makes the stannous chloride less easily decomposed by hydrolysis, and thus enables it to penetrate the material better. It also makes the dyeing slower by keeping the colouring-matter in solution, while when hard water is used it prevents the precipitation of the mordant. But a large excess of free acid must not be present. Cochineal crimson is dyed by mordanting the wool with from 4 to 8 per cent. of aluminium sulphate and 5 per cent. of cream of tartar, and, after mordanting, dyeing with 8 to 15 per cent. of cochineal. Single-bath methods also may be used. For example, after mordanting, the wool is lifted, the cochineal added, and the bath boiled up to dissolve it. The wool is then returned, and the bath boiled again for half an hour.

Cochineal is used also in the form of *ammoniacal cochineal*. This is made by allowing ammonia (3 parts) to stand in contact with cochineal (1 part) for about three weeks. About 50 per cent. of precipitated aluminium hydroxide is then added, and the mixture evaporated and portioned into cakes. Ammoniacal cochineal is used like cochineal, but the best mordant is tin. It gives bluer shades than cochineal. When the ammonia is driven off without the addition of aluminium hydroxide and the mixture evaporated to a paste, the product is termed *carminamide*. It is probable that ammoniacal cochineal consists of carminic acid in which a hydroxyl has been replaced by an amino group. Carmine and carmine lake, used as pigments, are respectively an aluminium calcium compound of carminic acid, and an aluminium or aluminium-tin lake of cochineal.

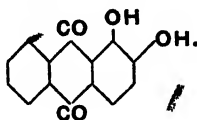
**Kermes** is rather similar to cochineal, being the dried bodies of a female beetle, and it is one of the oldest dyestuffs known. It contains a colouring-matter, *kermesic acid*,  $C_{18}H_{12}O_8$ , which is very similar to carminic acid in properties. Kermes is used in the same way as cochineal, but it does not give such good colours.

**Lac dye** is another dye obtained from an insect, which lives on the twigs of certain trees. When these twigs are broken off, still covered with the insects, they form *stick-lac*. When the twigs are removed, the product is *lac*, or *lac dye*. Shellac is a by-product in its manufacture. Lac dye, when added to cochineal, increases the fastness of the colour. It gives satisfactory colours only on a tin mordant. The colouring-matter is difficult to dissolve. The lac is ground to a paste with the stannous chloride and a little hydrochloric acid, and allowed to stand for some hours before use. It is used in the same way as cochineal.

**Madder**.—Formerly few natural dyestuffs were of greater importance than madder, owing to its use in dyeing Turkey red. It is the pounded root of the madder plant. Its chief colouring-matter is alizarine, which is present as a glucoside, *ruberythric acid*,  $C_{26}H_{28}O_{14}$ , together with other subsidiary colouring-matters in small quantities. Among the latter are purpurine and pseudo-purpurine. Synthetic alizarine has now superseded natural madder. When madder is allowed to ferment, the ruberythric acid is split up into alizarine and glucose:

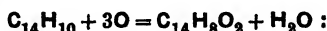


**Alizarine** is 1:2-dihydroxy-anthraquinone, and has the formula

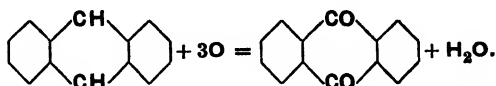


It is thus a derivative of anthracene, and its synthesis starts from this body.

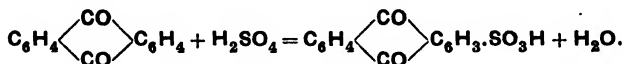
When anthracene is oxidized with sodium dichromate and sulphuric acid, anthraquinone is formed:



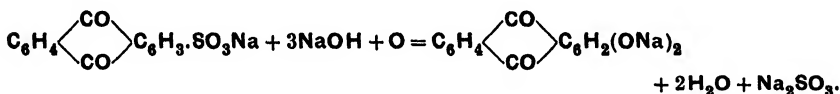
or



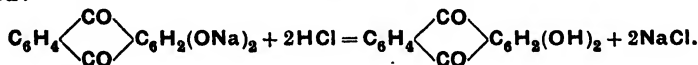
The anthraquinone is treated with its own weight of anhydro-sulphuric acid, i.e. sulphuric acid containing 50 per cent. of sulphur dioxide, at 160° C. This converts it into anthraquinone- $\beta$ -sulphonic acid:



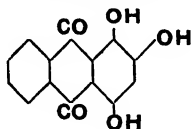
The sodium salt of this acid is next prepared. This is fused with sodium hydroxide and a little potassium chlorate, when a sodium salt of alizarine is formed:



When this salt, termed "sodium alizarate," is treated with an acid, alizarine is liberated:

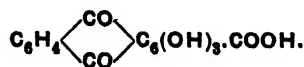


**Purpurine** is 1:2:4-trihydroxy-anthraquinone,



existing as a glucoside in madder root. It is also prepared synthetically. It dyes wool mordanted with aluminium a red colour with a bluish shade, and cotton a scarlet-red.

**Pseudopurpurine** is a trihydroxy-carboxylic acid of anthraquinone, represented by the formula

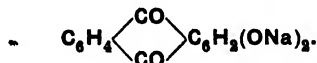


It occurs with purpurine in madder. It has no value as a dyestuff alone.

Synthetic alizarine may contain small quantities of purpurine or an isomeric form, *isopurpurine* or *anthrapurpurine*, 1:2:7-trihydroxy-anthraquinone. Alizarine GF and GFX (B.) are mixtures of alizarine with purpurine. These



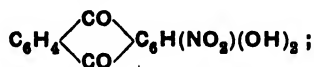
have yellow and blue shades. Alizarine crystallizes as dark red prisms which melt at  $289^{\circ}$  to  $290^{\circ}$  C., and sublime when heated above this temperature. It is insoluble in water or cold alcohol, but dissolves in the latter solvent when boiling, giving a yellowish-red solution. It dissolves in solutions of sodium hydroxide, giving a violet solution containing sodium alizarate,



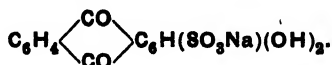
When heated with acetic anhydride, a diacetate,  $\text{C}_{14}\text{H}_6\text{O}_9(\text{OOC.CH}_3)_2$ , is formed; and when reduced with zinc dust, alizarine gives anthracene. With sulphuric acid alizarine gives a yellowish-red solution, which gives an orange-yellow precipitate when diluted with water. Alizarine is sold generally in the form of a paste containing 20 per cent. of the dyestuff. It is polygenetic, giving the following colours with different mordants:—

Aluminium . . . . .	Red
Tin . . . . .	Pink
Iron . . . . .	Violet
Chromium . . . . .	Puce-brown
Copper . . . . .	Yellowish-brown

*Turkey-red on cotton* is obtained by dyeing alizarine on Turkey-red oil and alumina in the presence of calcium acetate. Alizarine is generally dyed on wool on an aluminium or a chromium mordant. The presence of calcium acetate or other soluble calcium salt is an essential condition to obtaining good colours with alizarine, probably owing to the formation of a double lake, e.g. of calcium and aluminium. Since alizarine is insoluble in water, the paste is ground up with water, and poured into the dye-bath through a fine sieve. Bisulphite compounds are much more soluble in water, and still more soluble derivatives are obtained by such processes as nitration and sulphonation. Thus Alizarine Brown (B.) is a nitro compound:



Alizarine Carmine a sulphonate:



**Application of Alizarine to Wool.**—The goods are mordanted with either alum or potassium dichromate. For the former from 6 to 10 per cent. of aluminium sulphate and 5 to 8 per cent. of potassium hydrogen tartrate are used. The wool is entered into the bath cold, the temperature is raised gradually to the boiling-point, and the bath kept boiling for about half an hour. After washing, dyeing is carried out with 10 per cent. of alizarine paste (20 per cent.) and 4 per cent. of calcium acetate. Brighter shades are produced by adding from 1 to 4 per cent. of stannous chloride to the mordanting bath. The colour has an orange shade, depending on the amount of stannous chloride used. If the wool is mordanted with stannous chloride entirely, an orange shade very fast to light is obtained. For this purpose from 5 to 8 per cent. of both stannous chloride and potassium hydrogen tartrate are used, and the mordanted goods are washed and dyed as before.

To mordant with potassium dichromate, 3 per cent. of the substance is used,

either with or without 1 per cent. of sulphuric acid. Iron is also used as a mordant for alizarine on wool. From 4 to 8 per cent. of ferrous sulphate and the same quantity of potassium hydrogen tartrate are dissolved separately, and mixed for the mordanting bath. Alizarine can be mixed with many other mordant or natural dyestuffs to give a large range of fast compound colours. For a complete list of the derivatives of alizarine, together with their dyeing properties, the *Society of Dyers and Colourists' Colour Index* should be consulted.

**Application of Alizarine to Cotton.**—Alizarine is very difficult to dye on cotton and is little used except for Turkey-red. The following outline refers to one process of many, and is described by J. C. Cain, J. F. Thorpe, and R. P. Linstead, *The Synthetic Dyestuffs*, 7th edn., p. 410 (Griffin & Co.):—

After the cotton has been scoured by boiling with sodium carbonate solution and washing, it is worked, while still wet, in a bath containing 10 parts of Turkey-red oil to 90 of water. When saturated, it is squeezed, and dried at a temperature of 40° to 50° C. This operation is repeated twice, the cotton being dried between each immersion in the bath. The cotton is then worked in a bath of aluminium acetate (9° Tw.), wrung out, and dried at 40° to 50° C. This operation is then repeated. After this, it is worked at 30° to 40° C. in a bath containing 6 g. of ground chalk per litre of water. After half an hour it is removed, and washed thoroughly with water. It is then dyed with 15 per cent. of alizarine paste (20 per cent.) and, if the water is not hard, 4 per cent. of calcium acetate. The goods are entered at 20° to 25° C., and worked at this temperature for about 20 min. The bath is then heated slowly to 60° C., taking about 30 min. Dyeing is continued at this temperature for an hour, after which the goods are wrung out and dried. The dried and dyed cotton is then steamed at atmospheric pressure for two hours, or at a pressure of 2 atmospheres for one hour. After steaming, it is washed well, and brightened by heating with a 0.5 per cent. solution of soap in water at a pressure of 1.5 atmospheres for 10 min., then washing well, and drying.

This process may be simplified by heating the dye-bath to boiling; subsequent steaming then becomes unnecessary. However, the brighter shades of red are obtained at the lower temperature.

## CHAPTER XXXI.

### ANILINE BLACK AND OTHER COLOURS PRODUCED ON THE FIBRE BY OXIDATION.

**ANILINE** Black is the most important member of this class. It is not a dye-stuff in the ordinary sense of the word: it cannot be brought into solution and applied in a dye-bath. It has to be built up on the fibre from aniline, just as the naphthol dyes are from naphthol, but in the case of aniline black the process is one of oxidation, which causes the gradual condensation of aniline molecules. Aniline black is very largely used, particularly for cotton. It is the fastest black known, withstanding even moderate bleaching. The starting-point in its preparation is aniline hydrochloride (or *aniline salt*). The goods are treated with a solution of this salt, and are then oxidized by means of an oxidizing agent, such as potassium dichromate, in the presence of an oxygen-carrier. The oxidation appears to take place in three definite stages: first, Blue Indamine  $\text{NH} : \text{C}_6\text{H}_4 : \text{N} . \text{C}_6\text{H}_4 . \text{NH}_2$  is produced, then a green body termed *emeraldine*; this, when further oxidized, gives a black-coloured compound known as *nigraniline*; although black, this is readily reconverted into emeraldine by reducing agents; when, however, it is still further oxidized, *ungreenable aniline black* is obtained.

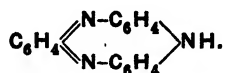
Emeraldine is a violet-blue base giving green salts. It may be prepared by suspending 14.4 g. of aniline in 300 ml. of water and neutralizing carefully with hydrochloric acid. From 9 to 10 ml. more hydrochloric acid are added, and a drop of a syrupy solution of vanadium chloride. The solution is cooled, mixed with a cold solution of 8.4 g. of sodium chlorate in 60 ml. of water, and the mixture kept at  $0.5^\circ \text{C}$ . for about forty hours. The emeraldine hydrochloride which is formed is filtered off, washed with water, and then treated with an excess of dilute ammonia to precipitate the base. This is filtered off and washed.

Emeraldine may be converted into nigraniline by allowing it to stand in contact with dilute ammonia containing about 3 per cent. of hydrogen peroxide. Nigraniline is a dark-blue base which forms blue salts. Ungreenable aniline black can be obtained from nigraniline by suspending 2.43 g. of nigraniline in a cold solution of 4 g. of aniline hydrochloride in 50 ml. of water, and adding slowly a solution of 1 g. of 75 per cent. chromic acid in 50 ml. of water. The precipitate is filtered off, washed, treated with ammonia, and dried, when it forms a black powder.

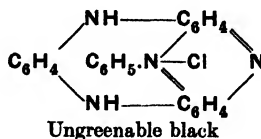
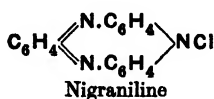
There is some doubt as to the constitution of aniline black. The empirical formula of ungreenable black is  $\text{C}_{66}\text{H}_{48}\text{N}_{11}\text{Cl}_5$ . It contains 15.5 per cent. of nitrogen, and aniline black on cotton can be estimated from a Kjeldahl nitrogen determination.

Commercial aniline blacks may contain, in addition to true aniline black, both nigraniline and emeraldine. Nigraniline is reduced to emeraldine by sulphurous acid, but ungreenable black is not, being converted only into a leuco

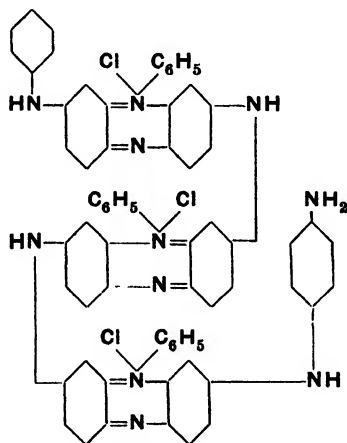
compound by hydrosulphites, from which the black is regenerated by oxidation. Green (*J. Soc. Chem. Ind.*, 1909, 28, 700) assigns the following structure to emeraldine:—



Whilst nigraniline is derived from emeraldine by the removal of hydrogen, and can readily be converted into emeraldine by reduction, ungreenable black is probably not a product of further oxidation, but a condensation product with aniline. The probable formulæ are—



Ungreenable black is thus a phenyl-phenazonium salt. The following formula is given for this compound in the *Society of Dyers and Colourists' Colour Index* (p. 217), from which the description of the preparation of emeraldine and nigraniline is also taken:—



Aniline black is used for all kinds of fibres. Although it is very fast, it has certain disadvantages, viz.—

(1) Cotton is liable to be tendered during the dyeing process, or subsequently if not thoroughly washed. This is due to the formation of oxycellulose, due to the action of the oxidizing agent and oxygen-carrier used.

(2) If the oxidation is not carried far enough, the black is liable to turn green owing to the formation of emeraldine.

(3) Bronzy or rusty shades of black are liable to be obtained.

(4) The colour may not be fast to rubbing.

**Methods of Dyeing.**—There are three distinct methods of dyeing aniline black, viz.—

(1) *Single-bath Aniline Black.*—In this process the aniline hydrochloride, oxidizing agent (potassium dichromate), oxygen-carrier (ferrous sulphate or copper sulphate), and hydrochloric or sulphuric acid are all dissolved and mixed in the dye-bath. The goods are then introduced into the cold liquor, and, after working for some time, the temperature is raised gradually to 140° F.

(60° C.). This is the simplest and cheapest process, but the least reliable. The colour is liable to rub and to become bronzy or greenish in tone, and is not very fast to bleaching. The method is very largely used for cotton, since it is less likely to cause tendering than the others.

(2) *Aged Aniline Black*.—In this method the oxidation is carried out in stages. The goods are padded with a mixture of aniline hydrochloride, an oxidizing agent (sodium chlorate), an oxygen-carrier (copper sulphate), and a deliquescent agent (ammonium chloride). They are then dried, and placed in a warm, moist atmosphere till the aniline has been changed into emeraldine. When this change is complete, the goods are transferred to a bath of potassium dichromate and sulphuric acid, in which the emeraldine is further oxidized to ungreenable aniline black. This method gives much better and faster blacks than the single-bath process. It is more suitable for wool than cotton, since with the latter oxycellulose may be produced during the ageing operation.

(3) *Steamed Aniline Black*.—In this method the goods are padded as before with the aniline hydrochloride, oxidizing agent, and oxygen-carrier; but the ageing is carried out at a much higher temperature by means of steam. This shortens the time to a few minutes. The oxidation of the emeraldine is completed in the same way as for aged aniline black. This method is commonly used for printing, but not much for dyeing.

(4) *Green's patent process* forms a fourth class. It seeks to avoid the danger of tendering by dispensing with the use of strong mineral acids and powerful oxidizing agents, the ageing being carried out by atmospheric oxygen alone. The method is thus suitable for cotton. It depends on the fact that small quantities of para-diamines (e.g. *p*-phenylenediamine) in the presence of an oxygen-carrier, such as copper chloride, make the oxidation of aniline possible at ordinary temperatures by mere exposure to air. Even the final oxidation by means of potassium dichromate and sulphuric acid may be dispensed with. The para-diamine acts as a catalytic agent, accelerating the action of the oxygen-carrier. The first stage of the reaction is the formation of Blue Indamine,  $\text{NH}_2\text{C}_6\text{H}_4\text{:N.C}_6\text{H}_4\text{.NH}_2$ , which then undergoes further condensation with aniline, giving complex indamines, from which emeraldine is formed by splitting off the para-diamine. The latter is thus regenerated, and is able to enter into reaction with more aniline. As an example: A padding mixture is prepared with 50 parts of aniline, 4 parts of *p*-phenylenediamine, and 30 parts of formic acid, with or without 48 parts of cupric chloride. The goods are then aged by exposure to moist air, by warm air, or by steam.

**Examples of Dyeing Processes.**—The number of processes for dyeing aniline black is very large. Nearly every dyer has his own particular formula. Moreover, great experience is required to apply any formula successfully. Knowledge alone is insufficient, although, of course, very helpful. The following are examples of the methods used:—

**Single-bath Aniline Black.**—The shade of black produced by single-bath processes may vary from blue-black, dead black, to bronzy black. In fact, bronzy shades are somewhat difficult to avoid without experience. This is because the result is affected by many factors, such as the amount of aniline used, the concentration and final temperature of the bath, the nature of the acid, and the after-treatment. The black is liable to rub, and is not fast to bleaching. As a general rule, when hydrochloric acid alone is used, a bluish-black is produced; while sulphuric acid tends to give bronzy shades. A mixture of the two acids gives a more jet-like black.

About 8 per cent. of aniline is required for a full shade, but the quantity recommended in different formulæ varies very widely, from 4.5 to 24 per cent.

Taking 8 per cent. of aniline, however, there would be required also: potassium dichromate, 10 per cent.; hydrochloric acid, 15 per cent. (32° Tw.); and copper sulphate, 1 to 2 per cent. The dichromate is dissolved first, and put into the bath; the oxygen-carrier (copper sulphate or iron liquor) is then dissolved separately, and added. The aniline is dissolved in the hydrochloric acid in a separate vessel, and is not added to the bath till immediately before the cotton is entered. The goods are wetted, and put into the cold bath. After working in this for about half an hour, the temperature is raised slowly to about 160° F. (71·1° C.), or sometimes to the boiling-point. But it must be remembered that by raising it to the boiling-point a somewhat different shade is produced. The dyed cotton is then thoroughly washed, and then treated with olive-oil emulsion or simply soaped, to brighten the shade and to remove any loose dye from the surface. The washing is an extremely important part of the operation. If any dichromate or oxygen-carrier is left in cotton goods, they invariably become tendered on keeping.

Another common type of formula contains equal quantities of hydrochloric and sulphuric acids, while ferrous acetate (iron liquor 20° to 38° Tw.) replaces copper sulphate as the oxygen-carrier; for example:—

Aniline oil . . . . .	5 to 10 per cent.
Hydrochloric acid . . . . .	5 „ 10 „
Sulphuric acid . . . . .	5 „ 10 „
Iron liquor . . . . .	5 „ 10 „
Potassium dichromate . . . . .	10 „ 20 „

J. M. Matthews (*Application of Dyestuffs to Textiles, Paper, Leather, and Other Materials*, p. 453) gives the following directions for producing an ungreenable jet-black: For 100 lb. of cotton two solutions are required, viz. (i) 12 lb. of aniline, 18 lb. of hydrochloric acid, and 24 lb. of sulphuric acid in 45 gallons of water; (ii) 24 lb. of potassium dichromate in 45 gallons of water. These are mixed together cold in equal volumes. The yarn is steeped in the mixture, 2 lb. at a time, till a bronzy black colour is produced. It is then wrung out, steamed for 20 min. at 3½ lb. pressure, and soaped.

Single-bath aniline black is used sometimes for topping direct blacks. The following is an example of the process: The dyed goods are worked in a cold bath containing 3 per cent. of aniline hydrochloride, 4 per cent. of potassium dichromate, 2 per cent. of ferrous sulphate, 4 per cent. of sulphuric acid, and 4 per cent. of hydrochloric acid. After working for half an hour the temperature of the bath is raised gradually to 160° F. (71·1° C.), and kept at this value for an hour. The goods are then squeezed, washed, exposed to air for a time, and finally soaped.

**Aged Aniline Black.**—This gives a much better black than the single-bath process, being much faster and ungreenable. In using it for cotton, care must be taken to avoid over-oxidation and tendering, due to oxycellulose.

In this method the goods are impregnated or padded with a solution containing the following: (i) aniline hydrochloride; (ii) an oxidizing agent, which is nearly always sodium chlorate; (iii) an oxygen-carrier, such as copper sulphate, ferrous sulphate, or vanadium chloride; (iv) a hygroscopic body, such as ammonium chloride. For each part of aniline hydrochloride about 0·3 to 0·5 of sodium chlorate is required.

The quantity of oxygen-carrier varies with the substance. One part of vanadium chloride is sufficient for 67,000 of aniline hydrochloride, but this salt is not used very much, as it acts too rapidly. With copper sulphate 1 part is required for 10 of aniline hydrochloride.

In making up the padding mixture, the aniline is first dissolved in a very slight excess of hydrochloric acid. But no free acid must be present, or the cotton would be quickly tendered during ageing. The excess of hydrochloric acid is therefore neutralized by the cautious addition of aniline. The remaining ingredients are then dissolved separately, and added to the solution. Again the proportions used are very variable. The following is an example of a formula recommended by the Badische Anilin- und Soda-Fabrik:—

Aniline hydrochloride . . . . .	60.0 lb.
Sodium chlorate . . . . .	20.0 „
Copper sulphate . . . . .	7.5 „
Ammonium chloride . . . . .	2.0 „
Aluminium acetate (15° Tw.) . . . . .	1.5 gallons
Starch (previously boiled with water) . . . . .	2.5 lb.
Water . . . . .	55.0 gallons.

The bath is used at a specific gravity of from 7° to 8° Tw.

The goods are worked in this solution at ordinary temperatures, then wrung out, and hydro-extracted. In the case of yarn it is better to do small lots

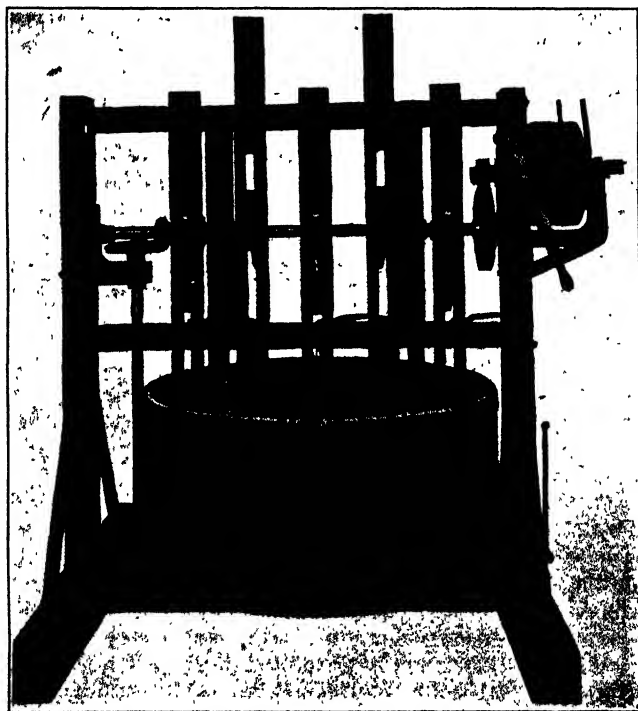


Fig. 187.—Smith Drum Padding ("Tom-tom") Machine.

(say 2 lb.) at a time, and no special apparatus is required. When dealing with large quantities a special machine, known as a "tom-tom," may be employed (Fig. 187); this forces the liquor into the goods by means of hammers.

After hydro-extraction the cotton is dried at a low temperature (95° F., 35° C.), being turned frequently to avoid uneven distribution of the padding

liquor. The operation can be carried out in an ordinary drying chamber or stove, or on a rotating frame or drum. When the goods are dry, steam is passed into the chamber until the temperatures shown by a wet- and dry-bulb thermometer are approximately  $T_w = 86^\circ \text{ F. (} 30^\circ \text{ C.)}$  and  $T_d = 95^\circ \text{ F. (} 35^\circ \text{ C.)}$ . These temperatures are maintained for about six hours, or until the goods have acquired the characteristic colour of emeraldine. They are then removed from the chamber, and chromed to convert the emeraldine into aniline black. For this a bath containing 4 per cent. of potassium dichromate and 1 per cent. of sulphuric acid is used, the goods being worked in it at  $180^\circ \text{ F. (} 82.2^\circ \text{ C.)}$  for 15 min. In order to obtain an ungreenable black it seems necessary that a little unoxidized aniline should be present during chroming. Small quantities of aniline hydrochloride, up to 0.5 per cent., are sometimes added to ensure this. But it is very important that no free aniline should be left in the finished goods, since it is liable to volatilize and form pink stains in white goods nearby. After the chroming, the goods are washed and soaped as usual for blacks. It is said that when aniline nitrate is substituted for the hydrochloride, after-chroming is unnecessary.

**Steamed Aniline Black.**—This method gives the fastest blacks, and there is also less liability of greening, or tendering, the cotton. The process is, however, employed more for printing than for dyeing. The goods are padded with a solution of aniline hydrochloride, oxidizing agent, and oxygen-carrier, as in the last process, but potassium ferrocyanide is commonly used as the oxygen-carrier. A suitable padding liquor may be made by dissolving separately 75 parts of aniline hydrochloride, 35 of sodium chlorate, and 40 of potassium ferrocyanide, mixing the solutions, and diluting to 1000 parts with water. The goods are treated with this solution, and dried evenly at a low temperature. They are then steamed for from 3 to 5 min., and chromed as before for from 15 to 30 min. in a solution of dichromate containing 1 part to 500 of water. Steamed aniline black requires more chroming than aged aniline.

**Detection of Aniline Black on Cotton.**—Since aniline black is often used in conjunction with other blacks, its detection is of some importance. It is changed, in many cases, to green emeraldine by sulphurous acid. The detection of oxidizing agents or oxygen-carriers is also of assistance. Aniline black is not dissolved by boiling with 1 per cent. sulphuric acid, nor does it give sulphuretted hydrogen when heated with hydrochloric acid and stannous chloride, but the fabric becomes brown. It is not stripped by a boiling solution of sodium sulphide. It does not bleed when boiled with soap and water and a piece of undyed mercerized cotton. When boiled with bleaching powder solution of  $5^\circ \text{ Tw.}$  strength, the fibre becomes reddish-brown if dyed with aniline black.

**Application to Wool.**—According to Prudhomme (*J. Soc. Chem. Ind.*, 1920, 39, 104A) aniline black can be dyed on wool by the following process: The goods are mordanted in a bath containing 10 to 20 g. of chromic acid per litre, squeezed, washed, and dried. They are then impregnated with a cold solution of aniline and formic acid, squeezed, and aged. A ferric salt may be added to the mordanting bath.

**Diphenyl black** is produced from *p*-amino-diphenylamine by an ageing process in a similar manner to aniline black, but without chroming. If *p*-phenylene-diamine is used, Paramine Brown is obtained; while *o*-dianisidine gives Orthamine Brown.

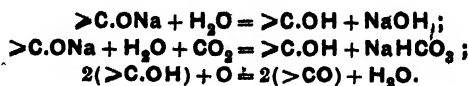


## CHAPTER XXXII.

### VAT DYESTUFFS.

THE vat dyestuffs are amongst the oldest of natural dyes. Indigo has been used in India from the earliest times of which there are historical records. The Egyptians also used it at least 3000 years ago. Julius Cæsar records that the Ancient Britons used woad for the purpose of staining their bodies and faces. Tyrian purple was manufactured and exported from Tyre nearly 4000 years ago. This dyestuff was obtained from shellfish, but indigo and woad are of vegetable origin, being prepared from the sap of plants, in which they exist as soluble colourless glucosides, *i.e.* substances which when decomposed give glucose as one product. The vat dyes are all characterized by one important property: they are insoluble in water, and hence cannot be used directly for dyeing. When they are treated with reducing agents, however, they combine with hydrogen, giving rise to leuco compounds. These leuco compounds are soluble in alkaline solutions, in which cotton and other textile fibres have a considerable affinity for them. When cotton containing these is exposed to air, the leuco compounds are oxidized, and insoluble colouring-matters are produced on the fibres.

The reduction of the coloured dyestuff to the leuco compound and the dissolution of the latter in an alkali were combined in one operation, which was carried out in a vessel known as a *vat*. This is the origin of the name *vat dyestuff*. Indigo was, until recently, the only vat dye of importance, and was derived entirely from the indigo plant. The preparation of synthetic indigo from coal-tar derivatives constituted one of the greatest chemical achievements at the end of the last century. The manufacture of this product on a commercial scale, from naphthalene, dates from about 1900. Since that time many other synthetic vat dyes have been discovered, and the dyer can now obtain a comparatively wide range of these colours. The vat dyes are somewhat complicated in structure and of several different types, but they are all characterized by containing a carbonyl group,  $>CO$ , which, when treated with reducing agents, combines with hydrogen to give  $>C.OH$ . These reduced compounds are the leuco compounds. They are insoluble in water, but react with caustic alkalis, forming soluble compounds of the type  $>C.ONa$ . When these are exposed to air, the leuco compound is reproduced, and is then oxidized to the insoluble dyestuff, thus:



Dyeing with a vat dyestuff involves three separate operations: (i) preparation of the *vat* or solution of the leuco compound, (ii) impregnation of the goods

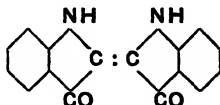
with the solution of the leuco compound, and (iii) oxidation of the leuco compound.

The vat dyestuffs may be divided into two groups: (i) the indigoids, and (ii) the anthraquinone vat dyes.

### (1) Indigoids.

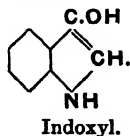
The indigoids include natural and synthetic indigo, and substituted indigos such as bromo- and thio-indigos. These are all characterized by forming pale yellow leuco compounds, which dissolve in weak solutions of sodium hydroxide. The leuco compounds are oxidized readily when exposed to air. All indigoids are soluble in boiling pyridine, and in many cases sublime on heating. They are suitable for both vegetable and animal fibres.

**Indigo**,  $C_{16}H_{10}O_2N_2$  or

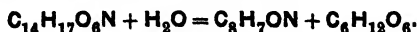


Until the beginning of the present century indigo was obtained exclusively from plants, mainly those of the genus *Indigofera*, which were cultivated chiefly in India. The knowledge of indigo and its properties spread gradually to Egypt and the intermediate countries, and thence to China some time during the seventh century. From Egypt the use of indigo was introduced into Greece and Rome, and finally became common in Europe during the fourteenth century. It reached England during the reign of Edward III, who introduced some Flemish dyers, and encouraged the cultivation of the indigo plant. Considerable opposition was offered to its use by the woad dyers and growers, who feared that it would ruin their trade. Both Henry IV and Queen Elizabeth made laws restricting or prohibiting its use.

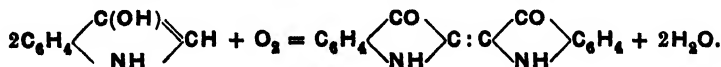
The indigo plant of India is known by the name of *Indigofera sumatrana*, but there are other varieties. It is grown each year from the seed sown during February. The plant reaches a height of about 3 ft., and it is gathered in August, when the colouring-matter content reaches its maximum (about 0.4 per cent.). The plant is not itself blue, nor are its juices, which are of normal greenish-yellow colour. The colouring-matter is present in the form of a soluble glucoside, known as *indican*, which is a combination of glucose and *indoxy*,



When this glucoside is decomposed by dilute acids or by enzyme action, it undergoes hydrolysis, glucose being one of the products of this reaction; the change may be represented by the equation:



This compound, indoxyl, when oxidized, gives insoluble *indigo blue*, or *indigotin*:



At the same time, small quantities of other vat dyes are produced. These are *indirubine*, a reddish-coloured dye, and *indigo brown*. A substance with no dyeing properties, termed *indigo gluten* or *indigo yellow*, is also precipitated.

The following is a brief outline of the details of manufacture. For fuller information, J. F. Thorpe and C. K. Ingold's *Synthetic Colouring Matters: Vat Colours* may be referred to. The plants are covered with water in steeping vats made of brick and lined with Portland cement. Each vat is about 4 ft. deep, and has a capacity of approximately 1000 cubic ft. The steeping is continued at atmospheric temperature till fermentation sets in, which is indicated by the evolution of gas. When effervescence has ceased, this operation is complete. The fermentation brings about the hydrolysis of the glucoside indican by means of enzymes produced by the bacteria present, yielding a sugar and indoxyl. The solution is run off into fresh vats, in which it is oxidized by means of air supplied by a revolving paddle. The colour of the liquid changes gradually from yellowish-green to deep blue, and ultimately a dark blue precipitate of indigotin is formed, together with some indirubine, indigo brown, and indigo gluten. The addition of an alkali, such as sodium hydroxide, lime, or ammonia, to the oxidizing vat assists the oxidation and makes the precipitate settle better. After the precipitated indigotin has settled, the clear liquor is drawn off. The sludge is then boiled with very dilute sulphuric acid, and then with water. After this, it is filtered, and the residue pressed into cakes and dried slowly by exposure to air.

*Natural indigo*, obtained by this process, is a hard blue substance, which gives a bronze-coloured streak when scratched. It contains from 60 to 65 per cent. of indigotin, together with small but variable quantities of indirubine, indigo brown, indigo gluten, and mineral matter. The indirubine is the most important of the secondary products. It should not exceed 2 per cent. Since it is a red colouring-matter, the shade of blue obtained with natural indigo is, to a certain extent, variable.

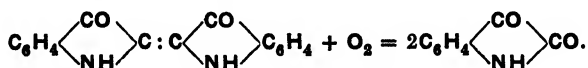
*Synthetic indigo* is a pure product containing 98 per cent. of indigotin. It is sold either as a powder or as a paste containing 20 per cent. of indigotin. Synthetic indirubine is also a commercial dye.

**Properties of Indigotin.**—Indigotin is insoluble in water, alcohol, dilute acids, and alkalis, but dissolves in boiling glacial acetic acid. It is slightly soluble in chloroform, amyl alcohol, and phenol, but the best solvents are boiling aniline and pyridine. It crystallizes from its solutions in these solvents in dark blue or purple needles. When heated to about 170° C. it sublimes, forming a purple vapour, which condenses again to form blue crystals of pure indigotin. If it is strongly heated in a closed vessel, either alone or with an alkali, aniline is produced as one product. When indigo is treated with concentrated sulphuric acid it dissolves, forming indigotin-sulphonic acids. There are four of these, produced by varying the conditions of sulphonation. The most important is indigotin-disulphonic acid,  $C_{16}H_8O_2N_2(SO_3H)_2$ , which is obtained by dissolving indigo in cold concentrated sulphuric acid:



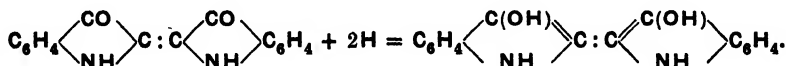
The sulphonic acid is soluble in water. If the solution in sulphuric acid is diluted, and saturated with salt, the sodium salt,  $C_{16}H_8O_2N_2(SO_3Na)_2$ , is precipitated. This sodium salt is *indigo carmine*, an important acid dyestuff. Solutions of indigo carmine form colourless leuco compounds when treated with reducing agents, as does indigo itself. These leuco compounds are re-oxidized to the original colour on exposure to air. When acted on by oxidizing agents, they give rise to sulphonic acids of isatin.

When indigotin is treated with oxidizing agents, such as nitric acid or potassium permanganate and sulphuric acid, it is oxidized to *isatin*:

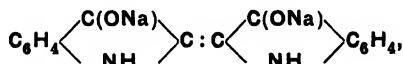


This reaction forms the basis of a common test for the presence of indigo on dyed cloth. Isatin is a soluble yellow substance, which dissolves in concentrated sulphuric acid, giving isatin-sulphonic acids.

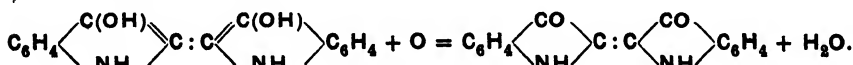
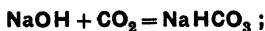
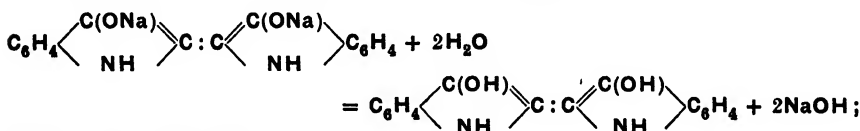
**Indigo White.**—The most important property of indigotin is the formation of a leuco compound, indigo white, when reduced in accordance with the equation:



Indigo white is insoluble in water, but forms a soluble compound,

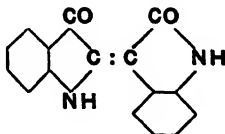


when treated with a solution of sodium hydroxide. When excess of alkali is present, a clear yellow solution is produced. When the solution is neutralized with acid, the indigo white is precipitated as a white powder. An excess of alkali is necessary to keep the leuco compound in solution since, like other sodium salts of phenolic compounds, it is hydrolysed readily. When the solution is exposed to air, the surface becomes covered with a layer of indigotin, produced by the action of carbon dioxide and oxygen in the following manner:



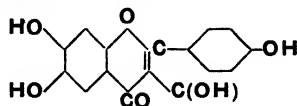
When oxidizing agents are added to the solution of indigo white, it becomes at first green, then blue, and finally a blue precipitate of indigotin is formed.

**Indirubine,**



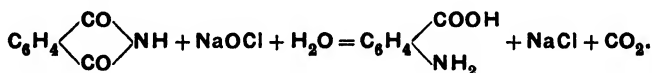
is a product of the secondary oxidation of indoxyl, and has properties similar to those of indigotin. It sublimes at  $340^\circ \text{C.}$ , is insoluble in water, and forms leuco compounds soluble in caustic alkalis, which dye textile fibres red. It is oxidized by potassium permanganate in the presence of sulphuric acid, but not so readily as indigotin. Like indigo it gives substitution products, such as bromindirubine. Thus Ciba Heliotrope B is a tetrabromindirubine.

*Indigo gluten, Indigo yellow*, is a trihydroxy-flavonol, of the formula

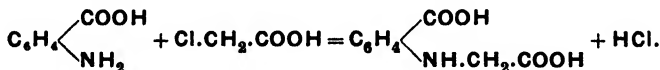


**Synthesis of Indigo.**—Natural indigo has now practically disappeared from the market, because at the beginning of the present century the Badische Anilin- und Soda-Fabrik manufactured and marketed synthetic indigo. The process was based on the following series of reactions:—

When naphthalene is oxidized by heating with sulphuric acid and a little mercury to act as an oxygen-carrier, it is changed to phthalic acid,  $C_6H_4(COOH)_2$ . This body when distilled gives phthalic anhydride,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown \end{smallmatrix} O$ . If phthalic anhydride is heated with ammonia under pressure, phthalimide,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown \end{smallmatrix} NH$ , is produced. This is next converted into anthranilic acid by treatment with sodium hypochlorite:



Anthranilic acid, when treated with chloroacetic acid, gives phenylglycine-*o*-carboxylic acid and hydrochloric acid:



When phenylglycine-*o*-carboxylic acid is fused with sodium hydroxide, indoxyl,  $C_6H_4 \begin{smallmatrix} \diagup C(OH) \\ \diagdown NH \end{smallmatrix} CH$ , is formed. When this is dissolved in water with addition of sodium hydroxide, and is subjected to the action of a current of air, it is oxidized to indigo blue (indigotin).

An improved method of manufacturing indigo synthetically has subsequently been introduced. The sodium salt of phenylglycine-*o*-carboxylic acid is fused with sodium hydroxide containing a small proportion of sodamide, when indoxyl is produced.

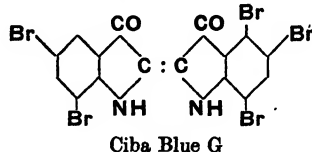
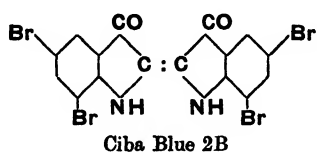
The fusion can be carried out at a lower temperature than in the method described above, with the result that a better yield of indigo is obtained. Further, benzene can be used as the starting material:



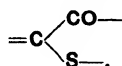
**Substituted Indigos.**—Bromindigos can be obtained from indigo by suspending it in acetic acid or some other suitable organic liquid, and then treating the suspension with bromine; in this way six atoms of bromine may be introduced. Chlorine substitution products are prepared in a similar way. In addition, substituted indigos containing two halogens may be obtained by the action of bromine on chlorinated indigos. In this way vat dyes such as Helindone Blue, Ciba Blue, and Durindone Blue are produced.

Increasing the number of bromine atoms causes a gradually increasing green shade, accompanied by a decreasing solubility of the leuco compound.

The commercial dyestuffs of this class are often mixtures of these brominated compounds. Ciba Blue 2B is chiefly tetrabromindigo, whilst Ciba Blue G contains five bromine atoms, as shown in the formulæ below:

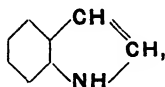


**The Thio-indigos.**—In these dyestuffs one or both of the NH-groups are replaced by a sulphur atom; thus the typical grouping is

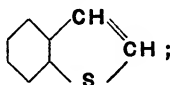


The thio-indigos and some ciba colours belong to this group.

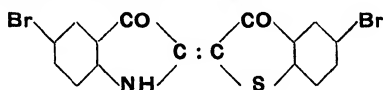
Ciba Violet 3B contains both an indole nucleus,



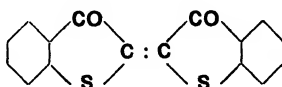
and a thionaphthen nucleus,



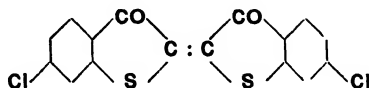
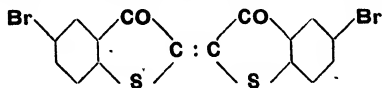
the dyestuff is represented by the formula



In Ciba Pink B there are two sulphur atoms:

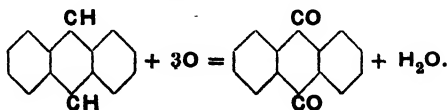


There are also substituted thio-indigos. Ciba Bordeaux B is a dibromo- and Ciba Red B a dichloro-thio-indigo:

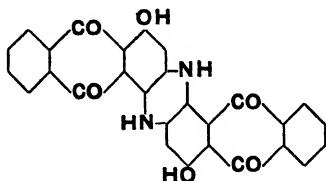


## (2) Anthraquinone Vat Dyes.

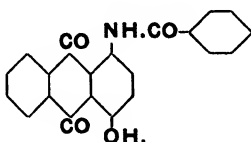
These are produced from anthraquinone, which is itself produced by the oxidation of anthracene. Anthraquinone may be made by treating anthracene with a mixture of sodium or potassium dichromate and sulphuric acid:



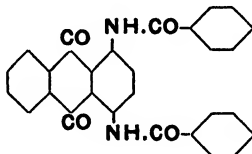
*Indanthrene Blue 5G* was the first dyestuff of this group to be placed on the market. It is obtained by fusing  $\beta$ -amino-anthraquinone with caustic soda. It has the structure shown in the formula:



The *Indanthrene*, *Algol*, and *Alizarine* vat dyes belong to this class. *Algol Pink B* is an example of a vat dye containing a typical anthraquinone grouping:

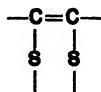


The *Duranthrene* colours comprise another class of vat dyes built upon the anthraquinone skeleton. An example is *Duranthrene Red 5G*, which has the structural formula:

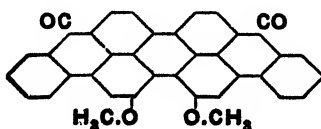


**Properties.**—These colours require a comparatively strongly alkaline solution to dissolve their leuco compounds, and are therefore not so suitable for animal fibres as for vegetable fibres. The leuco compounds are as a rule coloured. The dyestuffs do not (with few exceptions) sublime when heated, and are often sparingly soluble in pyridine, differing in both respects from indigoids.

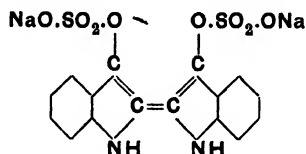
**Cibanone Derivatives.**—These are anthraquinone dyestuffs containing sulphur. Their structure is complex, but appears to consist of anthraquinone residues linked together by the grouping



**Perilene Vat Dyestuffs.**—The *Caledon* colours are perilene derivatives. Thus *Caledon Jade-green* contains two perilene residues, and has the formula



**Indigosols and Soledon Dyestuffs.**—These are sulphuric esters of leuco compounds of vat dyestuffs, *e.g.*



These compounds have a natural affinity for wool in a neutral or faintly acid bath, and thus obviate the danger of alkaline damage. The insoluble vat dyestuff is produced, after dyeing, by oxidation in a bath containing nitrous acid, potassium dichromate, or ferric chloride.

### Application of Vat Dyes.

**Indigo.**—The first thing in the dyeing of indigo is to prepare a vat, *i.e.* a solution of indigo white in an alkali. This consists essentially in reducing the indigo to its leuco compound in the presence of alkali. Stock vats are commonly made, which are diluted when required for dyeing. If solid indigo is used, it must first be ground to a very fine powder in a mechanical pestle and mortar or mill. The use of paste saves the trouble of grinding.

To-day sodium hydrosulphite is universally employed as the reducing agent. The fermentation vat, copperas vat, and zinc-lime vat, which were commonly used in the past, are now of only historical interest.

(1) *Fermentation Vat.*—In this, bacteria are used which produce reducing enzymes and nascent hydrogen, the indigo white being dissolved generally in lime-water, *i.e.* calcium hydroxide. In such a vat there must be present (i) reducing bacteria, (ii) food for the bacteria, and (iii) alkali to neutralize acids such as lactic and butyric, which are also produced, and to dissolve the indigo white as it is formed.

The reducing organisms are supplied by macerated woad or madder; food, by both of these and some bran; while the necessary alkalinity is maintained by an excess of slaked lime, which is dissolved gradually by the water. Other bodies, such as glucose, which is itself a reducing agent, are frequently added. The formulæ for this kind of vat are very variable. The following is an example given by E. Knecht, C. Rawson, and R. Loewenthal (*A Manual of Dyeing*, 9th edn., 1, 321—Griffin & Co.):

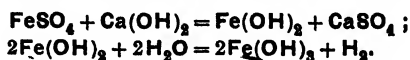
Indigo (60 per cent.)	.	.	.	.	20 to 40 lb.
Woad	.	.	.	.	5 „ 10 cwt.
Bran or sharps	.	.	.	.	30 „ 40 lb.
Madder	.	.	.	.	10 „ 15 „
Lime	.	.	.	.	12 „ 25 „
Water	.	.	.	.	2700 gallons.

The woad is first crushed, mixed with water in the bath at about 60° C., and allowed to stand overnight. The other ingredients are then added, and the bath is covered over to keep it warm, being stirred from time to time. In about three days the indigo will be reduced and dissolved, giving a clear yellow solution with a copper-like scum where it is exposed to the air. The fermentation vat is the oldest method, but is not used very much now.

(2) *Copperas Vat.*—In this, ferrous sulphate is the reducing agent and lime the solvent. When ferrous sulphate is treated with lime-water, ferrous

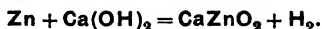


hydroxide is precipitated. This readily takes up oxygen, becoming changed into ferric hydroxide, and in the presence of water hydrogen is liberated:



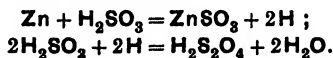
The indigo is ground into a paste with water, and then mixed with lime previously made into a cream with water. The ferrous sulphate is dissolved separately, and stirred into the mixture. The temperature is kept at about 60° C., and the mixture frequently stirred till the indigo has completely dissolved. Each pound of indigo paste requires about 3.5 of lime, 2.5 of ferrous sulphate, and 60 (i.e. 6 gallons) of water. This vat naturally contains a large quantity of precipitated iron hydroxide and undissolved lime, which is rather inconvenient. Some of the indigo is also lost, owing to the formation of adsorption compounds with the ferric hydroxide.

(3) *Zinc-Lime Vat*.—When zinc dust is mixed with milk of lime, it dissolves, forming calcium zincate and liberating hydrogen:

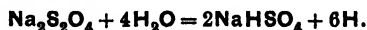


In preparing the vat the hydrogen thus liberated is used as the reducing agent, the leuco compound dissolving in the excess of lime-water. This vat produces a less bulky precipitate than the copperas vat, and there is less loss of indigo. For each pound of indigo paste (20 per cent.) 2 oz. of zinc dust and 5 lb. of quicklime are required. The indigo is made into a cream with the zinc dust, and, after dilution, the lime is added as milk of lime. The mixture is kept at 60° C., and frequently stirred.

**Hydrosulphite Vat**.—A solution of sodium hydrosulphite may be prepared from sulphurous acid or sodium bisulphite by reducing it with zinc dust. The latter is first dissolved with the liberation of nascent hydrogen, which reduces the sulphurous to hydrosulphurous acid:



The hydrosulphurous acid is then neutralized by the zinc, giving the zinc salt,  $\text{ZnS}_2\text{O}_4$ . The sodium salt can be obtained by precipitation of the zinc as zinc hydroxide by the addition of sodium hydroxide. Sodium hydrosulphite is a powerful reducing agent, and acts in an alkaline solution, being itself oxidized to sodium bisulphate:



Sodium hydrosulphite, made in this way, was formerly used in the preparation of vats in the presence of excess of either lime or sodium hydroxide. It is now replaced, however, by solid commercial sodium hydrosulphite. When this is used with sodium hydroxide, there is no precipitate and practically no loss of indigo. A stock vat may be made in the following manner: 10 lb. of indigo paste (20 per cent.) is mixed with 2 gallons of water. To this 2.5 lb. of sodium hydrosulphite is added gradually, with constant stirring, and then 5 pints of caustic soda solution of 76° Tw. The mixture is kept at about 60° C. and stirred frequently. Complete reduction is generally obtained in about 2 hours.

**Application of Indigo to Cotton**.—Cotton is generally dyed with indigo at ordinary temperatures. It should be boiled with caustic soda solution and scoured before dyeing. The dye-bath is first filled with soft water, and the dissolved oxygen removed by adding a little of the reducing agent used in the

preparation of the vat. In the case of sodium hydrosulphite about 1 oz. for every 100 gallons is sufficient. The reduced indigo is then added from the stock vat. The goods are dipped in the liquor for about 15 min. The material is next lifted out, the excess liquor is squeezed back into the dye-bath, and the goods are exposed to the air to allow the reduced indigo to oxidize. This sequence of operations is repeated till a shade of the required depth has been produced. A deep shade can be obtained only by successive dips into a comparatively weak solution. If too concentrated a solution is used, the colour is not fixed firmly, and is liable to be rubbed off easily. If, however, a series of vats of increasing strengths is employed, and, commencing with the weakest, the goods are dipped successively into the others, each of which is more concentrated than that preceding it, a deep shade of good fastness may be obtained. The first vat might, for example, contain 0.3 g. of reduced indigo per litre, rising gradually to 3 or 4 g. per litre in the sixth or last. When a series of vats is used, as the one with the lowest concentration is exhausted it is replaced by the next, and all the others are moved down, the last being replaced by a freshly prepared liquor. The dyed goods are finally washed with water, and soaped. While yarn is commonly dyed by immersion and hanging out, piece-goods are more conveniently treated in some form of continuous machine.

**Application of Indigo to Wool.**—Wool is dyed similarly to cotton, but it has no affinity for the reduced indigo in a cold bath, and penetration is also difficult; hence it is generally dyed at about 100° to 140° F. (37.8°–60° C.). Since wool is readily damaged by alkalis, the alkalinity of the baths must be kept as low as possible, particularly in view of the fact that the dyeing is carried out at a somewhat elevated temperature. Penetration may be assisted by squeezing, and the goods usually remain in the bath at each dip nearly twice as long as cotton. Dye vats containing ammonia, instead of a stronger alkali, in the presence of glue are very suitable for animal fibres. Like cotton, the wool should be freshly scoured, since absolute permeability is necessary. Wool dyed with indigo is often topped with other dyes, or indigo may be dyed on a bottom of a cheaper dyestuff. *Wooded blacks*, produced by topping indigo with logwood, have been described already (p. 427).

**Fastness of Vat Dyestuffs.**—Since the vat dyes are insoluble, they are among the fastest known dyestuffs. Many of them are fast to light, washing, alkalis, acids, stoving, and even bleaching.

**The Durindone colours** are indigoids. They include several blues and reds. The vats are made with caustic soda solution and sodium hydrosulphite powder. The colours have good fastness to acids, alkalis, cross-dyeing, moderate washing, and light, while some are fast to chlorine. In order to prepare the leuco compound solution, for each pound of dyestuff paste there are required 2.5 pints of caustic soda solution (76° Tw.) and 1.5 lb. of sodium hydrosulphite powder. The following dyeing instructions are given:—

Both for dissolving the colours and for dyeing, soft water should be used. If this is unobtainable, 1 lb. of soda-ash should be added to each 100 gallons of water. In preparing the dye-bath the water is run in, and the caustic soda (and soda-ash if necessary) is added. The temperature of the bath is raised to 120° F. (48.9° C.), and any lime salts which rise to the surface are skimmed off, after which the hydrosulphite powder is stirred in. The dyestuff is made into a thin paste with warm water, and passed into the bath through a fine sieve. The liquid in the bath is then stirred gently for about 10 min., or till the dyestuff is completely dissolved. For pale shades the bath is filled with water to about two-thirds of its capacity. The temperature is raised to 120° F. (48.9° C.), the dyestuff dissolved in the manner described above, and the bath

then filled with cold water, the final temperature being adjusted to 100° F. (37·8° C.). More level results are obtained by dyeing at this temperature. Any foam on the surface of the dye liquor is skimmed off. The boiled-out cotton is then entered, and worked for from 30 to 45 min. in the dye liquor. It is then squeezed, rinsed in cold water, and hung out to oxidize, giving it one turn during the process. When the colour is fully oxidized, the yarn is given four turns in a boiling soap bath containing about 2 lb. of soap, and then rinsed in warm water.

- **Anthraquinone Vat Colours.**—These are represented by the Duranthrene and other colours. They include yellow, orange, brown, red, green, and blue. These dyestuffs are, as a rule, very fast, some being capable of withstanding an ordinary bleaching process. As noted above, their leuco compounds require, however, a rather concentrated alkaline bath to hold them in solution. For this reason these colours are more suitable for vegetable than for animal fibres. With some of them the leuco compound is oxidized at 80° F. (26·7° C.) by means of a bath containing sodium dichromate and hydrochloric acid, or sodium perborate.

**Indigosols.**—The indigosols can be used for all fibres, and are suitable in many cases for mixtures of two or more, some of them giving solid or almost solid shades, as is seen in Table LX.

TABLE LX.—DYEING OF MIXTURES WITH INDIGOSOLS.

Dyestuff.	Fibres (50 per cent. of each).	Shade.
Indigosol pink IR extra . . .	Silk and wool	Almost exactly solid
Indigosol violet AZB . . .	Viscose rayon and wool	Almost solid
Indigosol O . . .	Silk and cotton	" "
Indigosol O . . .	Silk and mercerized cotton	" "
Indigosol OR . . .	Silk and mercerized cotton	" "
Indigosol HB . . .	Silk and viscose rayon	Silk paler than the viscose
Indigosol AZG . . .	Silk and wool	Almost solid
Indigosol green IB . . .	Silk and viscose rayon	" "
Indigosol green IB . . .	Silk and mercerized cotton	Exactly solid

Soledon Jade-green is a typical member of the class, and may be used for all fibres. The dye paste is sieved into the dye-bath, and 20 per cent. of Glauber's salt or 10 per cent. of sodium chloride is added. As a general rule, the shorter the bath the greater will be the degree of exhaustion. Dyeing is commenced at 60° C. and continued for 30 min., during which time the temperature is raised to 80° C. After dyeing at this temperature for 30 min., the goods are removed, squeezed, rinsed in cold water, and developed. In the case of wool the temperature may be raised to the boiling-point, and exhaustion completed, finally, by the addition of a little acid; but the addition of acid at the beginning of the dyeing is not desirable.

Development can be effected by the following methods: (i) immersion for one minute in a cold 1 per cent. solution of sodium nitrite, followed, after squeezing, by passing into cold 1 per cent. hydrochloric or sulphuric acid; (ii) immersion in a cold 1 per cent. solution of potassium persulphate and 1 per cent. of sulphuric acid; or (iii) immersion in a cold acidified 1 per cent. solution of ferric chloride.

The developed goods are washed with water, and soaped in a bath containing 10 lb. of soap and 5 lb. of sodium perborate in 100 gallons of water.

**Detection of Vat Dyes.**—Vat dyestuffs in general can be detected by warming them with a mixture of sodium hydrosulphite and sodium hydroxide. They all dissolve, and from the colour of the solution obtained some idea of the type of vat dye present may be obtained.

The following points may be noted:—

(1) Indigo<sup>oid</sup> dyestuffs give pale yellow solutions, sublime when heated, and dissolve in boiling aniline or pyridine.

(2) Anthracene derivatives give coloured solutions, and do not as a rule sublime, though they are soluble in aniline or pyridine.

**Identification and Estimation of Indigo on Textile Fabrics.**—When an indigo-dyed fabric is treated with a spot of nitric acid, a yellow spot of isatin with a greenish periphery is produced. But this reaction is given also by many other dyestuffs. Most of the other dyestuffs used with indigo are removed or altered by boiling dilute hydrochloric acid, while indigo remains unchanged. A small piece of the material when heated carefully in a dry test-tube will give violet vapours which condense again on the upper, cooler portion of the tube, forming a blue ring of indigo. None of these tests are altogether satisfactory. But indigo may be detected with certainty and estimated at the same time by Green's process (*Analysis of Dyestuffs*, p. 80):—

The sample is dried, and extracted with boiling pyridine in a continuous extractor chamber (Fig. 118, p. 264) till no more colour can be removed. This requires generally about two hours. The extractor flask is cooled, when the greater part of the indigo crystallizes out. Precipitation is completed by adding about 100 ml. of 50 per cent. alcohol, and the precipitate is filtered off on a weighed Gooch crucible, previously washed with all the solvents and liquids used in the analysis. The precipitate is washed successively with (i) hot 50 per cent. alcohol, (ii) hot 2 per cent. sodium hydroxide, (iii) hot 1 per cent. hydrochloric acid, (iv) hot water, (v) alcohol, and (vi) ether. This treatment will remove all other dyestuffs except indigo. The crucible is dried at 110° C., and weighed. The dried precipitate should be a bronzy crystalline powder, a dull appearance indicating the presence of impurities.

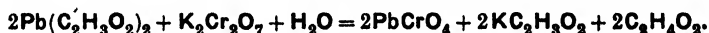
Instead of weighing the indigo, it may be converted into sulphonic acid and titrated with potassium permanganate, or this process may be used to check the purity of the dried precipitate. The crucible is transferred to a small beaker containing from 15 to 20 ml. of pure sulphuric acid. The beaker is warmed for 45 min. to 70° or 80° C. The solution is then carefully washed into a 500-ml. flask, cooled, and made up to the mark with distilled water. A portion is then largely diluted with water, and titrated with 0.02N. potassium permanganate. Each millilitre used corresponds to 0.00147 g. of indigo.

## CHAPTER XXXIII.

### THE MINERAL PIGMENTS.

MINERAL pigments are not dyestuffs but inorganic compounds, insoluble in water, and precipitated on the fibre by suitable double decompositions. They have no affinity for textile fibres, and are merely mechanically retained. Hence the operation of colouring fabrics by these pigments cannot strictly be said to be dyeing. But since some of them are basic oxides, which act as mordants, they may be shaded or topped with suitable coal-tar dyestuffs. The mineral pigments are used chiefly for cotton, though Prussian blue has been mentioned in connection with the dyeing and weighting of silk. Among the more common are the following:—

**Chrome Yellow.**—This colour consists of precipitated lead chromate,  $\text{PbCrO}_4$ . This compound occurs native. Both this and manufactured lead chromate are used for paints. The colour is dyed on cotton by first impregnating it with a solution of a soluble lead salt, such as lead acetate, and then working the impregnated material in a hot dilute solution of potassium dichromate. The reaction with lead acetate is expressed by the equation:



That is, potassium acetate and acetic acid are simultaneously produced. Lead chromate is insoluble in water or acetic acid, while potassium acetate dissolves in both; hence, if the goods are washed, the by-products are removed.

A 5 per cent. solution of lead acetate may be used. After the cotton has been saturated with this, it is squeezed, passed into a hot 1 per cent. solution of potassium dichromate, and then washed thoroughly.

**Chrome Orange.**—If the dyed cotton is passed through a bath of boiling milk of lime, the yellow colour is changed to orange, owing to the formation of a basic chromate. This colour is known as *chrome orange*. Its composition is represented by the formula  $\text{PbO} \cdot \text{PbCrO}_4$ , or  $\text{Pb}_2\text{CrO}_5$ . The reaction is



The calcium chromate is soluble in water, and can be washed away. Chrome orange is produced also if sodium hydroxide is added to the potassium dichromate bath:



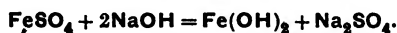
Chrome orange may be produced also from calcium plumbite. When lead acetate solution is treated with milk of lime, a solution of calcium plumbite,  $\text{CaPbO}_2$ , is obtained. After allowing the excess of lime to settle, the clear liquor is drawn off for use. The cotton is soaked in this solution, and then, after squeezing, worked in a lukewarm bath containing 5 per cent. of potassium dichromate and 1 per cent. of sulphuric acid. After further rinsing, it is worked

in a bath of boiling milk of lime till the full colour is developed, and then washed and dried.

Chrome yellow is very fast to light, washing, and acids. Alkalis turn it orange, and it becomes black when exposed to sulphuretted hydrogen owing to the formation of lead sulphide. Chrome orange is fast to alkalis, light, and washing, but not to acids.

**Iron Buff.**—This consists of a hydrated ferric oxide. It is produced in two ways:—

(1) The goods are saturated with a 5 per cent. solution of ferrous sulphate, squeezed, and soaked in a hot 5 per cent. solution of sodium hydroxide or carbonate. This precipitates ferrous hydroxide in accordance with the equation:

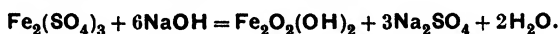


The goods are then washed, and exposed to the air, whereby the ferrous hydroxide becomes oxidized to hydrated ferric oxide; thus:



When the oxidation is complete, the goods are washed and dried. The oxidation can be accelerated by immersing the goods in a cold solution of bleaching powder of 1° Tw. strength. But this must be followed by very thorough washing, or the cotton will be tendered.

(2) Ferric sulphate may be used instead of the ferrous salt, in which case no oxidation is necessary, but only washing:



Iron buffs are fast to light, washing, and alkalis, but are sensitive to acids.

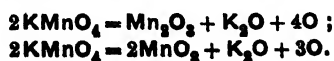
**Chrome Green** consists of chromium sesquioxide,  $\text{Cr}_2\text{O}_3$ . The goods are soaked in a 5 to 10 per cent. solution of a soluble chromium salt, such as the sulphate or chrome alum, and, after squeezing, passed into a boiling bath of sodium carbonate. Wool can be dyed by any of the methods used for mordanting with chromium. For example, it may be boiled in a solution of potassium dichromate with or without sulphuric acid, and then reduced with sodium bisulphite.

**Mineral Khaki.**—Iron buff combined with chrome green gives a khaki colour, the particular shade produced depending upon the proportions of the constituents used. The cotton is padded with a solution containing ferrous sulphate and chrome alum, and then treated with a boiling solution of sodium carbonate. After washing, it is exposed to air to oxidize the ferrous hydroxide to hydrated ferric oxide.

**Manganese Brown or Bistre.**—This colour may be obtained in two ways:

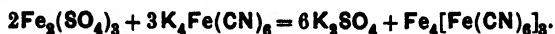
(1) The cotton is soaked in a 5 per cent. solution of manganous chloride,  $\text{MnCl}_2$ . After squeezing, it is then passed into a cold bath of 5 per cent. sodium hydroxide. This precipitates manganous hydroxide,  $\text{Mn(OH)}_2$ . This is then oxidized to manganese sesquioxide,  $\text{Mn}_2\text{O}_3$ , by treating the goods with a dilute solution of bleaching powder (1° Tw.). After this, the dyed cotton is washed thoroughly.

(2) The material is soaked in a dilute solution of potassium permanganate till the desired brown shade is produced. It is then well washed, and dried. This method gives a mixture of the oxides  $\text{MnO}_2$  and  $\text{Mn}_2\text{O}_3$ ; thus:

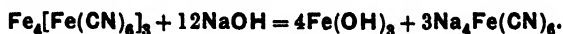


The potassium oxide,  $K_2O$ , reacts with the water to form potassium hydroxide, which is washed away.

**Prussian Blue,  $Fe_4[Fe(CN)_6]_3$ .**—Cotton may be dyed with Prussian blue by first producing iron buff, as described above, and then soaking it in a solution of potassium ferrocyanide and dilute sulphuric acid. This change may be represented by the equation:



It must be remembered that Prussian blue is at once decomposed by alkalis with the formation of ferric hydroxide:



After treatment with potassium ferrocyanide, the dyed goods are washed and dried.

Purple shades of Prussian blue can be produced by padding with a mixture of iron salts and stannous chloride. For example, the cotton is soaked at  $30^\circ C$ . in a warm bath of basic ferric sulphate of  $5^\circ Tw.$  strength, containing from 2 to 5 per cent. of stannous chloride. It is then squeezed, and worked, as before, in an acidified solution of potassium ferrocyanide.

Wool is dyed in a different manner. Either potassium ferrocyanide or ferricyanide may be used, but the latter gives the better results. The wool is soaked for 15 min. in a cold bath containing 10 per cent. of potassium ferricyanide,  $K_3Fe(CN)_6$ , and 20 per cent. of sulphuric acid. After 15 min. the temperature of the bath is raised gradually to the boiling-point. Some of the ferricyanide becomes reduced to ferrous sulphate, and ferrous salts give with excess of potassium ferricyanide a precipitate of Turnbull's blue, which is thought to be the same as Prussian blue. If nitric acid is used, potassium ferrocyanide may replace the ferricyanide. In this case some ferric salt is produced by the oxidizing action of the nitric acid, and thus Prussian blue is formed. Or, as an alternative, potassium ferrocyanide and sulphuric acid may be used, and a little nitric acid added during the dyeing. The addition of from 1 to 5 per cent. of stannous chloride to the bath, either at the beginning or towards the end of the process, gives purplish shades, as with cotton. The wool may also be mordanted with stannous chloride before dyeing by the method already described (p. 421).

The application of Prussian blue to the weighting of silk has been described before (p. 430).

Prussian blue is fast to light and acids, but very sensitive to even mild alkalis.

## CHAPTER XXXIV.

### THE SCOURING, BLEACHING, AND DYEING OF ARTIFICIAL FIBRES OR RAYONS.

RAYON of all kinds requires special treatment in scouring, bleaching, or dyeing. It is very susceptible to both mechanical and chemical damage. Processes which would be safe to use with cotton would in many cases be quite unsuitable for rayon. Mechanical damage in a previous process always causes uneven dyeing. Friction, undue tension, and torsion all act in this way. The machines used for rayon should be as nearly frictionless as possible, and all the corners should be rounded off. When dyeing stockings, machines with vigorous movement, such as that given by a paddle, are liable to cause damage. The Smith Drum or machines in which movement is initiated by steam or air are preferable. Yarns are generally dyed by hand or in the Gerber type of machine. Fabrics have to be processed in a winch machine, although elliptical drums are used for acetate fabrics to avoid creases, as described in Chapter XXIV.

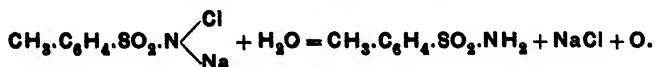
**Preliminary Treatment.**—Rayon goods often contain size, which in turn usually contains starch. When size is present, it should be removed by a preliminary *desizing* treatment. Several processes are available for this purpose, *viz.*:

(1) The goods are soaked at 60° C. in a solution of *diastase* containing about 1 per cent. on the weight of the goods, until no reaction for starch is given with iodine solution. They are then washed with water. It must be remembered that diastase does not act in an alkaline bath.

(2) Diastase can be replaced advantageously by *rapidase*, which is not affected by a moderate degree of alkalinity (*pH* 8), and can be used at a temperature of from 80° to 90° C. When a bath containing 2 lb. of rapidase in 50 gallons of water is used at 80° C., desizing is complete in a few minutes. The process may be made continuous, the goods being run through the desizing bath into a washing bath containing hot water.

(3) *Sodium perborate* changes starch into soluble starch, and simultaneously bleaches the rayon. A solution containing 2 g. of perborate and 3 g. of olive-oil soap per litre may be used at about 70° C. for 2 hours.

(4) *Aktivin* acts in the same way as perborate. From 0.1 to 0.3 per cent. per gallon of liquor is used, to which are added  $\frac{1}{2}$  oz. of soap and  $\frac{1}{2}$  oz. of sodium carbonate per gallon. The goods are digested in this liquor for about 2 hours at 70° to 80° C. The aktivin decomposes in accordance with the equation:



**Scouring.**—Water used in scouring should have zero hardness. Only olive-oil soap should be used, but assistants such as Turkey-red oil or sulphonated



wetting agents may be added to the bath, together with a little sodium carbonate. Sometimes immiscible organic solvents, such as toluene or tetralin, are used as assistants. The bath should contain from 2 to 5 g. of soap per litre, and the maximum temperature is 85° C. A boiling bath is liable to cause mechanical damage. After scouring, the goods are washed thoroughly and carefully with soft water.

**Bleaching.**—As noted above, a certain amount of bleaching may be accomplished during desizing. When bleaching is carried out as a separate process, sodium hypochlorite is used. Regenerated cellulose is very susceptible to over-bleaching, and 1 g. of chlorine per litre is the strongest solution that is safe to use. After bleaching, the goods are washed with water, treated with an aqueous solution of acetic acid (0.5 per cent.), then dechlorinated in a bath containing a little sodium sulphite, and washed until quite free from acid. Hydrogen peroxide may be used for bleaching in the same way as for silk, but stoving is totally unsuitable for any kind of rayon.

**Sercoop.**—This is produced if required in the same way as for silk.

## DYEING.

The different kinds of regenerated cellulose rayons have similar affinities for dyestuffs to those of cotton. The dyeing properties of cellulose acetate are, however, very different. Hence the two types must be considered separately.

### Dyeing Regenerated Cellulose Rayons.

**Basic Dyestuffs.**—Nitro, cuprammonium, and viscose rayons differ from cotton in having a distinct affinity for basic dyestuffs, that of nitro rayon being the greatest, probably on account of the presence of residual nitro groups. Pale shades can be produced on all of these by dyeing in a bath containing acetic acid in the same way as for silk. If dark shades are required, the goods must be mordanted with tannic acid or katanol. For example:—

The goods are soaked in a bath containing 2 to 5 per cent. of tannic acid for 3 or 4 hours at 100° F. (37.8° C.). They are then hydro-extracted carefully, soaked for half an hour in a cold bath containing 1 to 2.5 per cent. of potassium antimonyl tartrate, and then washed. Dyeing is started in a cold bath containing 2 per cent. of acetic acid. The solution of the basic dyestuff, previously strained or filtered, is added in portions, the temperature being raised gradually as with cotton. The dyed goods may be back-tanned if desired.

**Direct Dyestuffs.**—These dyestuffs are used very extensively for regenerated celluloses. The affinity of nitro rayon for direct dyestuffs is rather less than that of viscose and cuprammonium, because of the presence of residual nitrate groups. The direct dyestuffs are used in a short bath containing from 5 to 20 per cent. of Glauber's salt. Sodium chloride should not be used. Alternatively, a plain soap bath containing no Glauber's salt may be employed. As a general rule, it may be said that the less Glauber's salt is used, the more even will be the dyeing; and although regenerated cellulose can be dyed at low temperatures, the best results are obtained at a temperature of about 190° F. (87.8° C.).

**Defects.**—There are difficulties connected with dyeing, and defects are common. Thus, when dyeing with Chlorazol Sky-blue FF, the following may be observed: (i) some hanks may be dyed deeper or lighter than the correct shade; (ii) the same hank may show different shades outside and inside;

and (iii) individual hanks may show dark or light streaks, known as the *barré effect*. These faults may be due to (a) the yarn itself; (b) faults in winding, knitting, or weaving; (c) incomplete scouring, or over-bleaching; (d) faults in dyeing; and (e) the use of unsuitable dyestuffs. These will be considered briefly.

*The Yarn.*—Rayons consist of coagulated or precipitated colloidal solutions, each filament of colloidal micelles or complexes being interspersed with intermicellar spaces. The dyestuff complexes must be able to penetrate into these intermicellar spaces, and the size of the latter determines that of the dyestuff micelle which can penetrate the surface of the fibre. On the other hand, the size of the fibre micelle determines the quantity of dyestuff which can be fixed. These two factors depend largely on the degree of ripeness of the spinning solution. This in turn is measured by its viscosity. Unless a constant viscosity of the spinning solution is maintained, the affinity of the filament for dyestuffs will be variable. It may be said, however, that ripening is now a very carefully controlled process, and that dyeing faults are often due to the other causes named.

Uneven tension in winding, knitting, or weaving, or anything which causes torsion or stretching, is sure to give trouble in dyeing. Rough handling or surface friction acts in the same way, whilst imperfect scouring, or the presence of oxidized oil which is not removed by scouring, inhibits penetration of the dye liquor.

*Use of Unsuitable Dyestuffs.*—Wilson (*J. Soc. Chem. Ind.*, 1920, 39, 322r) found that dyestuffs having a low molecular weight dye viscose more evenly than those of the same class which have a high molecular weight, as is illustrated by Table LXI. Whittaker (*J. Soc. Dyers Col.*, 1926, 42, 86) showed

TABLE LXI.—EFFECT OF MOLECULAR WEIGHT ON DYEING PROPERTIES.

Dye.	Molecular Weight.	Dyeing Properties.
Rosophenine 10B . .	600	Even
Indoine blue . .	521	Even
Diamine green . .	812	Fairly even
Dianil sky-blue . .	992	Very uneven

that those direct dyestuffs which exhibit the least capillary attraction in solution, or have a low surface tension, dye viscose the most evenly. Soap lowers surface tension, and thus assists even dyeing. The colloidal nature of the dyestuff is important also. The more readily soluble a direct dyestuff is, the more likely is it to give uneven dyeings. Thus Whittaker (*Dyer and Calico Printer*, 1927, p. 206) states that Chlorazol Sky-blue FF, Chloramine Fast Green BL, Chloramine Black BH, and Chrysophenine 2G are four of the worst colours for accentuating "barriness" but yet are extremely soluble. Dyestuffs which dye quickly minimize "barriness," because they dye before differences in affinity of the viscose have time to exercise their effect. All direct dyestuffs give colloidal solutions. It is probable that the difference between an even and an uneven dyeing dyestuff lies in the size of the ultimate particles, or the degree of dispersion. Some dyestuffs which dye unevenly at low temperatures dye evenly at 90° C.. Dialysis experiments prove that at high temperatures molecular aggregates are broken down. Thus, it seems that

"even" dyeing results when the dye particles are able to penetrate the intercellular spaces easily.

The action of surface tension is illustrated by the following experiment (Trotman, *Dyer and Calico Printer*, 1930, p. 160). When alcohol is added to a cold aqueous solution of chrysophenine, the surface tension of the liquid is increased. As this increases, the affinity of the dyestuff for viscose diminishes gradually, until a point is reached at which the viscose remains undyed. On the other hand, the affinity of cotton for the dyestuff remains unchanged, and in a mixture of viscose and cotton the former is left undyed.

*Selection of Direct Dyestuffs.*—It is evident that only those dyestuffs should be used which are known to be even dyers, and this is particularly important when two or more are required. The following tests are used to distinguish "even" from "uneven" dyers:—

*Capillary Test.*—Two equal lengths of viscose twist are suspended vertically with their lower ends immersed in a bath containing 0.4 g. of dyestuff, 0.2 g. of soap, and 1 g. of Glauber's salt in 400 ml. of water, at a temperature of 60° C. After 15 min. the length of the undyed portion of the twist is measured. Dyestuffs which give high numbers dye viscose evenly, those with low numbers unevenly. When using two or more dyestuffs together, those with similar dyeing numbers should be chosen.

*Temperature-range Test.*—The capillary test has now been abandoned in favour of the temperature-range test, which depends upon the facts that dyestuffs showing a maximum affinity for viscose at 20° C. give the most even results in large-scale work, whilst those showing maximum affinity at 90° C. give the most uneven results. Eight small skeins of equal weight are wound from the same skein of viscose. Sufficient dye liquor is made for nine dye-baths, the volume of liquor to viscose in each bath being 40 : 1. The percentage of the various dyestuffs tested is based on a 0.5 per cent. sky-blue FF shade, so as to give approximately the same depth of shade at 90° C. The assistants used are 2 per cent. of soap and 10 per cent. of Glauber's salt. The dyestuff, soap, and Glauber's salt are boiled up in half the total volume of dye liquor, and the remaining half-volume added as cold water. Eight dye-baths are filled from the bulk, the same volume being used for each, and are cooled or heated to the requisite temperature. The test skeins are dyed for 30 min. in the eight dye-baths at the following range of temperatures: 20°, 30°, 40°, 50°, 60°, 70°, 80°, and 90° C.

Some dyestuffs, such as Chrysophenine G and Icyl Orange G, show a maximum affinity at 20° C., which becomes gradually less as the temperature rises. Others, such as Chloramine Fast Green BL, show a minimum affinity at 20° C., but the affinity increases with rise of temperature to a maximum at 90° C., while still others, such as Brilliant Benzo Green B, give a maximum affinity at 50° to 60° C., the affinity decreasing at higher and lower temperatures. Those dyestuffs which show a maximum affinity at 20° C. are the most even, those with the maximum affinity at 90° C. the most uneven, dyers. The rule for choosing dyestuffs for compound colours is to select those which show a maximum affinity at 20° C. or at some higher temperature.

*Equalizing-power Test.*—For this test a dye-bath containing 2 per cent. of soap on the weight of the viscose is used. Two equal weights of viscose are dyed together in a second bath. One dyed sample and an equal weight of undyed viscose are boiled for half an hour in the soap bath. High-number dyestuffs will go on to the undyed sample until both have the same colour, whilst with low-number dyestuffs the undyed sample remains practically undyed.

**Time of Half-dyeing Test.**—Boulton and Reading (*J. Soc. Dyers Col.*, 1934, 50, 381; 1938, 54, 268) recommended that the speed with which a direct dyestuff dyes viscose rayon should be used as a test for suitability for this purpose, instead of the temperature-range test. The dyeing rate, as expressed by the time required for standard exhaustion of a standard bath, measures the levelness of a dyestuff. Those which dye most rapidly give the most level shades. The choice of dyestuffs for mixtures should be guided by dyeing speed, satisfactory mixtures being those whose constituents have the same rate of exhaustion.

Standard quantities of a standard viscose rayon yarn are dyed for various times from a few seconds to 16 hours, or more in some cases, and, by colorimetric analysis of the progressively exhausted dye-baths, a graph of the

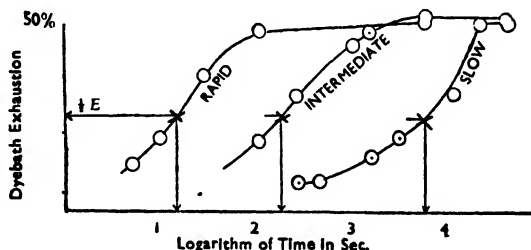


Fig. 188.—Curves showing Rate of Dyeing for Typical Direct Dyes.

increase of dye-absorption with time is plotted. Dyeings are carried out at exactly 90° C. with a liquor-viscose rayon ratio of 40 : 1 and with 0.5 per cent. of dye on the yarn weight. The amount of salt added to the test dye-baths is not standard for all dyes, but refers, in the case of each dye, to a fixed exhaustion value, i.e. 50 per cent. (to a close approximation) of the dye taken. From a logarithmic plot of the dye-absorption time graph, the time required for half-dyeing is read directly. It may be pointed out here that, whereas the time taken in reaching the *final* exhaustion value cannot, from consideration of the shape of the graph, be read off even approximately, the time required to attain *half* the final value can be read with considerable accuracy on a scale of the logarithm of the dyeing time in seconds.

All dyeing curves for the same yarn assume the same form. Fig. 188 shows rate-of-dyeing curves for some typical cases. The "time of half-

Type of Dye.	Dye.	Exhaustion, <i>E</i> .	<i>E</i> /2.	Logarithm of Time of Half-dyeing.	Time of Half-dyeing (min.).
Rapid . . .	Diazo brilliant orange GR	49.8	24.9	0.112	0.22
Intermediate	Visco copper blue EG	51.1	25.6	2.32	3.5
Slow . . .	Sirius supra green BL	50.0	25.0	3.78	100.4

dyeing" varies greatly with different direct dyestuffs. The value for Chlorazol Fast Orange GS is 0.07 min., and that for Chlorazol Fast Pink BKS 280 min. The original paper (*J. Soc. Dyers Col.*, 1938, 54, 268) gives a table of the half-dyeing times of a large number of direct dyestuffs, together with information about the selection of dyestuffs for mixtures.

**Level-dyeing Process.**—Messrs. Courtauld Ltd. found that the production of level shades on viscose is assisted by dyeing in the presence of a soluble inorganic salt of  $\beta$ -naphthol. Good results are obtained when the bath contains 1 per cent. of  $\beta$ -naphthol and 1 per cent. of salt, calculated on the weight of liquor, and dyeing is conducted at 90° C.

**Correction of Uneven Dyeing.**—Messrs. Courtauld Ltd. have suggested also a process for the correction of such faults as streaks or bars of light or dark colour on dyed viscose. The goods are worked for 30 min. at 90° C. in a bath containing 1 lb. of  $\beta$ -naphthol and 1 lb. of salt per 10 gallons of water. The naphthol does not dissolve completely, but floats in the form of crystals. After this treatment the goods are washed thoroughly with hot water or soap and water.

**After-treatment.**—The dyed rayon may be brightened by treatment with a weak solution of Turkey-red oil, monopol oil, or an olive-oil soap emulsion. The colours may be after-treated, diazotized and developed, or coupled with *p*-nitraniline by the methods used for cotton.

**Sulphur Dyestuffs.**—These are as a rule uneven dyers, only a few giving level colours. Moreover, the strongly alkaline bath which is used is likely to diminish lustre and tensile strength. The addition of a protective colloid, such as glue, to the dye-bath is helpful, and soap or soluble oil may be used also.

**Azoic Colours.**—These are dyed in the same way as for cotton, but "blinding" is apt to give trouble.

**Vat Dyestuffs.**—The vat dyestuffs are used largely for the production of fast colours. But they are not all suitable: like the direct dyestuffs, they may be divided into even and uneven dyers. The **even dyers** include the following:—

Algol blue 3R,	Duranthrene golden-orange Y,
Algol brilliant red 2B,	Duranthrene red R,
Algol pink R,	Duranthrene violet RR,
Caledon red BN,	Durindone blue 4B and 6B,
Caledon violet RN,	Hydron sky-blue FK,
Caledon brilliant purple 2R,	Hydron Bordeaux B,
Ciba blue 2B,	Hydron pink FB and FF,
Ciba grey G,	Hydron scarlet BB,
Ciba pink B,	Hydron orange R,
Ciba heliotrope B,	Indanthrene orange RRR,
Ciba red G,	Indanthrene brilliant violet BBK,
Ciba violet B and R,	Indanthrene yellow GK,
Cibanone brown V,	Indanthrene brown 3R,
Cibanone yellow R,	Indanthrene orange 3R,
Duranthrene red BN,	Indanthrene pink B,
Duranthrene Bordeaux R,	Paradone yellow AG new,
Duranthrene brilliant violet R,	Paradone brilliant violet R.
Duranthrene claret B,	

Evenness may be tested by the method of Hall (*Silk J.*, 1928, 53, 59). A quantity of viscose sufficient for a large number of tests is selected from one consignment, and half of this is treated with 5 per cent. sodium hydroxide solution for 4 hours at room temperature, washed, soured with acetic acid, washed, hydro-extracted, and dried. The even-dyeing colours will dye both alkali-treated and untreated viscose to about the same shade, but uneven dyers will show a greater affinity for the alkali-treated viscose.

The vat should be made in the following manner: Half of the total volume of water required is heated to 140° F. (60° C.), and the requisite quantities of caustic soda and hydrosulphite are added. The dyestuff is made into a paste with a little Turkey-red oil, then diluted with water, and passed through a sieve into the vat. When reduction is complete, the rest of the water is added; only soft water should be used. The goods are introduced at about 120° F. (48.9° C.); if hanks, they are hung on bent glass rods. The goods are then wrung out carefully and oxidized in air, hydrogen peroxide, or sodium perborate, according to the nature of the dyestuff. Finally, they are washed and soaped.

### Dyeing Acetyl Rayon.

**Suitable Direct and Basic Dyestuffs.**—Since acetyl silk is an ester of cellulose, one would expect that its affinity for dyestuffs would be different from that of cellulose. This is the case; and as the degree of acetylation increases, the affinity for direct dyestuffs decreases. Owing to the presence of acetyl groups, it has a direct affinity for bases and basic dyestuffs. The presence of sulphonic-acid groups as a rule prevents dyeing with a direct dyestuff. This is not, however, altogether true, since the British Dyestuffs Corporation (Brit. Pat. 226,940—1924) found that if the  $\text{SO}_3\text{H}$  group occupies the *ortho* position with respect to an azo group and, in the case of monazo dyestuffs, the *peri* position to an amino group, and no hydroxyl group is present, then the dyestuff has a direct affinity for cellulose acetate. Further, carboxyl groups do not act in the same manner as sulphonic-acid groups, carboxylated amino dyestuffs having generally a direct affinity for cellulose acetate. Such groups as hydroxyl, nitro, and nitroso, in the absence of sulphonic-acid groups, also confer affinity for cellulose acetate. These facts mean that, if only selected dyestuffs are used, the fibre can be dyed by the usual methods. Commercial acetyl rayon contains residual hydroxyl groups, and these in all probability explain the affinity for certain direct dyestuffs.

The results mentioned above led to the preparation of special ranges of dyestuffs for acetyl rayon, such as the *cellutyl* and *fast cellutyl* colours. The rayon is cleaned at 40° to 45° C. in a bath of soft water containing 2 per cent. of soap and 2 per cent. of ammonia or sodium carbonate for 15 to 20 min., and then washed with cold water. The dyestuff is made into a paste with cold water, and dissolved in hot water. In certain cases the water must not be boiling: these are—

Cellutyl red . . . . .	80° C.
Cellutyl sky blue . . . . .	80° C.
Cellutyl fast bright green B . . . . .	80° C.
Cellutyl fast bright green Y . . . . .	80° C.
Cellutyl fast yellow AB . . . . .	40° C.

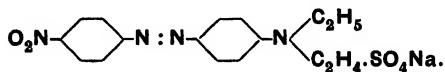
**The Dye-bath.**—The quantity of liquor should be from twenty-four to thirty times the weight of the rayon, *i.e.* from 2½ to 3 gallons per pound. The cleansed rayon is entered into the bath made up with the necessary quantities of dyestuff, salt, and acid at 70° to 75° C., and kept at this temperature for 30 min. A higher temperature detracts from the lustre of the rayon. After dyeing, the rayon is washed in warm soft water. In all but very light shades the goods should be soaped in a 0.25 per cent. solution of soap for from 10 to 15 min., and then washed off in warm soft water. The details below refer to both Cellutyl and other makes of dyestuffs.

Briggs (*J. Soc. Dyers Col.*, 1921, 37, 287) recommends the following method

of dyeing: After the rayon has been scoured in soap and ammonia as described above, it is washed in two different lots of water, soured in a bath containing 2.5 per cent. of hydrochloric acid (30 per cent.), and finally washed with water.

In dyeing, about 30 per cent. of sodium chloride is used as an assistant, but no acetic acid is necessary, except to neutralize the alkalinity of the water. Dyeing is started usually in a cold or lukewarm bath, the temperature being raised gradually to 65° or 75° C.; but at 75° C. the lustre of the silk is liable to be diminished. Dyeing is continued for about half an hour, after which the goods are rinsed in warm water, soaped lightly, washed, and finally brightened with dilute acetic or formic acid.

Certain monazo-sulphato dyestuffs dye acetyl rayon from a neutral or slightly alkaline bath; an unnamed example is



It is a scarlet dye (Perkin and Bate, B.P. 237,729—1924) made by coupling diazotized *p*-nitro-aniline with ethyl sodium sulphato-ethylaniline.

Some other methods, although now obsolete, have a historic interest. Briggs and Palmer (*J. Soc. Dyers Col.*, 1921, **37**, 153) found that the affinity for basic and direct dyestuffs was increased greatly by a preliminary treatment of the cellulose acetate with a swelling agent, such as ammonium thiocyanate. Clavel used magnesium chloride in the same way for basic dyestuffs. In another method (Brit. Pat. 215,373—1922), either pyridine, piperidine, or guanidine were suggested as assistants.

Burgess, Ledward, and Harrison (*J. Soc. Dyers Col.*, 1922, **38**, 229) made use of solutions of dyestuffs prepared by the addition of a precipitant in the presence of a protective colloid. The following examples are given:—

(a) *Basic dyestuffs*. One hundred grams of acetyl rayon is worked in a bath containing 2 g. of methylene blue and 2 g. of glue in 2 litres of water, the temperature being raised gradually to 80° C. A solution of 2 g. of sodium stannate in 200 ml. of water is then added gradually, the rayon being turned after each addition. When the desired shade is obtained, the rayon is rinsed and dried. Magenta may be dyed similarly, using 1 g. of saponin instead of glue and 2 g. of tannic acid instead of sodium stannate.

(b) *Direct dyestuffs*. Using 2 g. of Diamine Sky-blue in the glue bath described above, the goods are worked for 5 min. at 70° to 80° C., and 0.5 g. of dianisidine dissolved in 2 ml. of acetic acid and 200 ml. of water is added in small portions.

**Saponification Method.**—This was proposed by Cross, Briggs, and Richardson (B.P. 11,886—1920, and *J. Soc. Dyers Col.*, 1922, **38**, 169). Cellulose acetates are saponified by alkalis, with the formation of a salt of acetic acid and hydrated cellulose. If insufficient alkali (such as sodium hydroxide) for complete decomposition is used, this saponification can proceed in two ways: either (i) by uniformly lowering the acetyl value; or (ii) by complete saponification from the surface inwards, i.e. by forming an outer layer or sheath of regenerated cellulose, with an acetyl value increasing gradually from the periphery to the centre of the fibre. Since this regenerated cellulose has the same dyeing properties as other rayons, the second condition is that which is required. The affinity for dyestuffs is directly proportional to the quantity of alkali consumed. When a fibre dyed by this process is examined in cross-section under the microscope, it is seen to consist of a deeply dyed external sheath, the thickness of which is determined by the degree of saponification, and an

undyed core. The conditions favourable to high intensity of initial saponification are either a high temperature in the presence of dilute alkali, or a low temperature with a concentrated alkali. The saponification may be carried out previous to dyeing, but it is not essential; both saponification and dyeing can proceed simultaneously. By saponifying the rayon with 10 per cent. of its weight of sodium hydroxide at 75° C. the process can be regulated to give about 20 per cent. of regenerated cellulose and an inner core of 65 to 70 per cent. of unaltered cellulose acetate soluble in acetone. It should be noted that, if saponification proceeds too far, the characteristic properties of acetyl silk are lost.

The saponified product may be tested by the following method: It is extracted three times with ten times its weight of cuprammonium solution for two minutes. The united extracts are acidified to precipitate the dissolved regenerated cellulose. This is filtered off on a weighed Gooch crucible, washed, dried, and weighed. The unchanged cellulose acetate is extracted from a fresh sample by means of acetone, the solvent evaporated, and the residue dried and weighed.

For level dyeing, it is important that the saponification should proceed regularly. More even results are said (Sanderson, *J. Soc. Dyers Col.*, 1922, **38**, 162) to be obtained by preliminary saponification with alkali saturated with salt.

Small-scale experiments giving good results can be carried out as follows (Clayton, *J. Soc. Dyers Col.*, 1921, **37**, 303): The rayon is steeped for half an hour at 21° C., with gentle agitation, in a solution of sodium hydroxide containing 2.25 ml. of a 72° Tw. solution to 150 ml. of water. It is then washed in water, acidified with dilute hydrochloric acid, and finally washed again in water. Dyeing is started at 20° C., and the temperature raised gradually; but, as indicated above, dyeing and saponification can be carried out together in the dye-bath. Silicates, borates, or aluminates may be used instead of sodium hydroxide, and sodium acetate, from 1 to 2 per cent., is also recommended, since it gives very regular saponification.

The following methods of dyeing by the saponification process are given by L. G. Richardson:—

*Pre-treatment with Sodium Hydroxide.*—After scouring, the rayon is treated for 45 min. in a bath containing 100 times as much water as rayon, and one-tenth the weight of rayon of sodium hydroxide, at a temperature of 75° to 80° C. It is then washed, and dyed like cotton. The dye-bath should contain from 30 to 40 times as much water as rayon by weight (and sufficient soap to produce a permanent lather with light shades). Glauber's salt should not be used unless absolutely necessary. The dyeing should be started cold or lukewarm, and the temperature raised gradually to a maximum of 70° to 75° C.

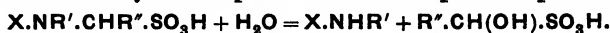
*Single-bath Process.*—Treating and dyeing in the same bath are carried out in exactly the same way, except that the dyestuff is added to the sodium-hydroxide bath.

*Ionamine Dyestuffs.*—The ionamines (Green, *J. Soc. Dyers Col.*, 1923, **39**, 10) are particularly adapted for dyeing acetyl rayon. According to Green, the dyeing of this appears to be mainly a solution phenomenon, depending upon the following factors: (i) The presence in the dyestuff of amino, substituted amino, or hydroxyl groups; but if strong salt-forming groups, such as the sulphonio-acid group, are also present, the affinity is lessened or destroyed. (ii) When basic dyestuffs are employed, their salts must be readily dissociated by water, since it is the base itself, and not the salt, which is absorbed by the fibre. (iii) The free base should be sparingly soluble in water.

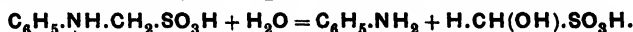


(iv) The molecule should not be too large, since complexity tends to diminish the solubility in non-aqueous solvents, and therefore also in the fibre substance. The methods of holding the base in solution by means of protective colloids or acids are inelastic, and are also unsuitable for acetyl rayon mixed with wool, cotton, or silk. The ionamines fulfil the above conditions. They are derived from  $\omega$ -sulphonic acids, i.e. sulphonic acids in which the  $\text{SO}_3\text{H}$  group is situated in the side-chain. They have the general formula  $\text{X.NR}'\text{.CHR}''\text{.SO}_3\text{H}$ , where  $\text{X}$  is an aryl nucleus, and  $\text{R}'$  and  $\text{R}''$  are alkyl groups, or-hydrogen.

As the  $\text{SO}_3\text{H}$  group is external to the nucleus, these compounds are readily hydrolysed by dilute acids or alkalis, but are comparatively stable in neutral solutions. When hydrolysed they give the corresponding amino compound, together with an aldehyde-bisulphite or its decomposition products; thus:

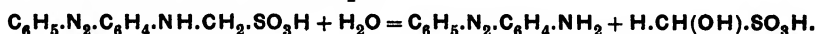


In the case of anilinemethyl- $\omega$ -sulphonic acid, the reaction is



The products being aniline and aldehyde-sulphurous acid, it seemed likely that if the hydrolysis of suitable dyestuffs containing the  $\omega$ -sulphonic-acid grouping were effected in the dye-bath in the presence of acetyl rayon, the latter would be dyed by the insoluble dyestuff base as it was liberated. Azo dyestuffs were built up whose solubility in water depended on the presence of the  $\omega$ -sulphonic-acid group, and all other sulphonic-acid groups were excluded. These dyestuffs were termed *ionamines*.

Ionamines are soluble in water, and behave in a similar manner to ordinary acid dyestuffs; but they dye acetyl rayon readily from a slightly acid or faintly alkaline bath. The dyed rayon, moreover, contains free amino groups, and can therefore be diazotized, and developed with phenols or amines. Thus the methyl- $\omega$ -sulphonic acid of aminoazobenzene gives on acetyl rayon aminoazobenzene, which can be developed:



The suitability is limited by two factors: (i) the  $\omega$ -sulphonic-acid compound must be readily soluble in water; and (ii) the hydrolysed base must be sufficiently soluble in cellulose acetate. It should be noted that the dyeing involves a chemical change, and is unlike the dyeing of cotton with direct dyes. Hence uneven shades cannot be made level by ordinary means, such as longer immersion in the dye-bath.

According to Green, the dyeing of acetyl rayon is in general most easily explained by the solution theory. Nearly all of the substances which dye it are soluble in benzene or a hydrocarbon solvent. This is illustrated by Ionamine A. If a cold aqueous solution of this dyestuff is shaken with benzene, the water becomes yellow, the benzene remaining colourless. But when warmed, the benzene becomes gradually yellow, and the water colourless. Acetyl rayon resembles benzene in that it absorbs but little water when wetted. Also the interface, like that of benzene-water, acts as a semipermeable membrane, permitting the passage of the base but not that of the aldehyde-bisulphite. Hence hydrolysis is accelerated, since the basic phase is continually removed by solution in the acetyl rayon, whilst the action of the interface as a semipermeable membrane in not allowing the aldehyde-bisulphite to follow prevents the establishment of an equilibrium, until practically the whole of the base has been absorbed by the silk. It is different in the case of wool. Here the water passes readily into the fibre, and the basic groups have a natural affinity for the  $\text{SO}_3\text{H}$  groups of the dyestuff. Hence the latter is taken

up as a whole, and hydrolysis is retarded. The affinity of ionamines for cotton varies inversely with that for acetyl rayon.

There are two classes of ionamines: (i) those containing one salt-forming group, typified by Ionamine B; and (ii) those containing two salt-forming groups, of which Ionamine A is an example. The first class has greater stability to hydrolysis, and is little affected when dyed with organic acids. The second class is more easily hydrolysed, and can be dyed by means of formic or oxalic acid, or in a faintly alkaline or neutral bath; hence these are not suitable for self-shades, but they can be developed.

**Application of Ionamines.**—Owing to the fact that uneven shades cannot be rectified, it is advisable to commence dyeing at a low temperature and to heat the bath gradually to about 65° C., at which temperature the maximum affinity is developed without damage to the lustre of the rayon. The concentration of the bath may vary within wide limits, from 20 to 100 times the weight of the rayon, without affecting the exhaustion. The addition of salt to the bath does not affect the exhaustion, and is not recommended, except in dyeing acetyl rayon and cotton unions with a mixture of an ionamine and a direct dyestuff. A neutral bath may be used, but hydrolysis is assisted by the presence of either an acid or an alkali. As a rule, 1 per cent. of either formic acid or sodium carbonate is used as an assistant. In dyeing twisted cord it is advisable to work the material in a neutral bath for some time before adding the acid.

*Diazotization and development* are carried out in the same way as with primuline. But more time is required, owing to the lower penetrability of acetyl rayon. The diazotizing bath is made up with 3 parts of sodium nitrite and 10 parts of hydrochloric acid in 1000 of water. Diazotization is usually complete in 5 min., and the rayon is washed till free from acid before developing. Only unsulphonated phenols or amines can be used as developers; the most useful are  $\beta$ -naphthol, resorcinol, and  $\beta$ -oxynaphthoic acid (2-hydroxy-3-naphthoic acid). The last-named is best for purple, blue, or black shades. It gives deeper and faster shades when used in a slightly acid solution. In making up the bath, the  $\beta$ -oxynaphthoic acid is dissolved with sodium carbonate or hydroxide (1 part in 300 of water), and then the solution is made faintly acid to litmus-paper by stirring in dilute acetic acid.  $\beta$ -Naphthol is used in a weakly alkaline solution, and resorcinol without any addition. Development is slow at ordinary temperatures, but is complete in 5 or 10 min. at a temperature of from 50° to 60° C. Table LXII shows the shades obtained with four ionamines. Rainbow effects may be obtained by dyeing with an ionamine and developing with mixed developers.

TABLE LXII.—DEVELOPMENT OF IONAMINES.

Developer.	Ionamine			
	A.	B.	H.	L.
Direct . . .	Yellow	Orange	Orange-yellow	Dull yellow
Resorcinol . . .	Reddish-brown	Reddish-orange	Reddish-brown	Purple-brown
$\beta$ -Naphthol . . .	Reddish-purple	Scarlet	Reddish-purple	Purple
$\beta$ -Oxynaphthoic acid	Navy blue to black	Crimson	Purple	Bright blue

Ionamines have no affinity for cotton or other rayons. They dye wool like ordinary acid dyestuffs, without undergoing hydrolysis, from an acid bath. Natural silk appears to be dyed by ionamines, partly in the hydrolysed and partly in the unhydrolysed condition. These varying dyeing affinities give the ionamines important uses in the dyeing of unions, either in producing solid shades, two-colour, or shot effects. Thus, in the case of unions of cotton or viscose with acetyl rayon, by selecting suitable direct dyestuffs and ionamines, both fibres can be dyed either a solid shade or different colours, or one can be left undyed, either in the same bath or by a two-bath process. For example, to obtain a deep solid black a single bath is used, containing a suitable diazotizable cotton black and Ionamine A. The dyeing is carried out at about 75° C. in the presence of 20 per cent. of salt. The goods are then diazotized, and developed with  $\beta$ -oxynaphthoic acid. Or the material can be dyed first with ionamine from an acidified bath, after which the reaction is made faintly alkaline with sodium carbonate, and the direct dye added. For a two-colour effect, Ionamine B and Chlorazol Sky-blue 2F can be used without subsequent diazotization, giving a blue colour on the cotton and an orange on the acetyl rayon. Or, if Ionamine L and primuline are used in a neutral or alkaline bath, and the primuline is then diazotized and developed with  $\beta$ -oxynaphthoic acid, then the acetyl rayon is dyed blue and the cotton bluish-red. Since ionamines dye wool in a similar manner to acid dyestuffs, unions of this fibre with acetyl rayon can be dyed with mixtures of ionamines and acid dyestuffs. Thus, with Ionamine B and Coomassie Navy-blue in an acid bath, the rayon is dyed orange and the wool navy-blue to black.

According to Green and Saunders (*J. Soc. Dyers Col.*, 1924, **40**, 138) the chief advantages of the ionamines are (i) ready solubility, and (ii) miscibility with direct dyestuffs, whereby a great range of solid colours can be obtained on cotton-acetyl-viscose mixtures. Thus Cellutyl Union Black R is a mixture of Direct Black and ionamine. When dyed on cotton unions and developed with  $\beta$ -oxynaphthoic acid, a fast solid black is obtained. Difficulties in dyeing are even penetration of twist or jumper cord and barriness.

**Dispersed Dyestuffs.**—The *duranol*, *dispersol*, and *celatene* dyestuffs consist of colloidal solutions or suspensions of derivatives of amino-anthraquinone, for which cellulose acetate has a direct affinity. These will dye acetyl rayon from a neutral bath at temperatures ranging from 110° to 180° F. (43.3°–82.2° C.). The following examples of Duranol colours are given by Messrs. I.C.I. Ltd. :—

1-Amino-anthraquinone . . . . .	Yellow
1-Amino-2-methylanthraquinone . . . . .	Yellow-orange
1-Methylanthraquinone . . . . .	Red
1 : 4-Diamino-anthraquinone . . . . .	Violet
1 : 5-Diamino-hydroxyanthraquinone (methylated at one or both amino groups) . . . . .	Crimson
4 : 8-Diamino-anthrarufine . . . . .	Sky-blue

**Application of Dispersed Dyestuffs.**—The following methods for dyeing are given by Messrs. I.C.I. Ltd. :—

The dyestuff paste is stirred up with water, and added to the warm dye-bath (110° to 120° F., 43.3°–48.9° C.), preferably through a fine sieve. The addition of a little soluble oil to the dye-bath assists in obtaining level results and good penetration, and in some instances appears to give clearer and brighter shades. The use of about 3 lb. of soluble oil per 100 gallons of dye-bath will be found sufficient for most purposes. It may be added separately to the dye-bath, or it may be stirred up with the colour paste. Soft water should be used if soluble

oil is to be added to the dye-bath. The addition of assistants to the dye-bath does not increase the exhaustion of the Duranol and Dispersol dyestuffs. The rayon is entered at about 110° to 120° F. (43.3°–48.9° C.), the temperature raised slowly to 180°–185° F. (43.3°–48.9° C.), and dyeing allowed to proceed for half an hour. Soap may be added to the bath instead of soluble oil, in which case the temperature of the dye-bath is kept down to 170° F. (76.7° C.). In the case of full shades, such as navy-blues and blacks, it is preferable to enter the material at 180° to 185° F. (82.2°–85.0° C.).

*Development of Dispersol Diazo Black AS Paste.*—This dyestuff is applied in the manner described above, but its direct shade is of no interest. The production of black necessitates diazotization and development with  $\beta$ -oxynaphthoic acid. The rinsed material is therefore treated for 20 to 30 min. in a cold bath containing 5 lb. of sodium nitrite and 10 pints of hydrochloric acid (32° Tw.) per 100 lb. of material. This is followed by thorough rinsing in cold water, after which development is carried out with either (a)  $\beta$ -oxynaphthoic acid or (b)  $\beta$ -oxynaphthoic acid S, as follows:—

(a) 5 lb. of  $\beta$ -oxynaphthoic acid are dissolved by boiling with one-third of its weight of soda-ash. This is added to the developing bath, which is brought up to 130° F. (54.4° C.), and 5 pints of acetic acid (30 per cent.) are added. The rayon is then entered, and development proceeds for half an hour at 130° F. (54.4° C.).

(b) 5 lb. of  $\beta$ -oxynaphthoic acid S are dissolved by boiling with water. This is added to the developing bath, which is brought to 130° F. (54.4° C.), and 3 pints of acetic acid (30 per cent.) are added. Development is then carried out as under (a).

It is most important that the developing bath should be definitely acid before the material is entered. It is equally important also that the developing process be completed. If the full time or quantity of developer is not allowed, there is danger of the process being incomplete and the resultant colour unstable, in which case the shade of the material is likely to become brownish after a few days. A simple test is to treat a small portion of the rayon in nearly boiling water (200° F., 93.3° C.) for about 15 min. If the shade is maintained a good black, there is little danger of a brownish tone developing later. If, however, the material turns brown, it shows that the colour is unstable and development incomplete.

*Hank-dyeing.*—Acetyl-rayon yarn is dyed over sticks in the open bath or in machines. The most common type of machine for yarn-dyeing is that in which the rayon is suspended on rollers which revolve eccentrically and reverse periodically.

Where very good light-fastness is essential, combinations of the following colours will be found most suitable for the production of the shades desired:

Duranol light yellow S paste,  
Duranol orange CS paste,  
Duranol orange GS paste.

Duranol red 2BS paste,  
Duranol violet 2RS paste,  
Duranol blue GS paste.

The difficulty most likely to be encountered in yarn-dyeing, particularly if turned by hand, is the rapid exhaustion of the colours. This, naturally, is most noticeable in light shades. It is therefore advisable when dyeing pale shades to work in a long liquor, as well as to make an addition of oil to the bath. For the purpose of securing adequate restraint, a 100 : 1 liquor will not be found too long.

*SRA Dyestuffs.*—These are similar to the Duranol dyestuffs, i.e. they consist of dispersions or suspensions of insoluble colouring-matters. The

emulsifying agent is a fatty acid, generally together with sulpho-ricinoleic acid. These dyestuffs are used in the following manner:—

The goods are scoured for from half an hour to an hour in a bath containing 1.25 to 1.5 g. of olive-oil soap and 1 ml. of 20 per cent. ammonia per litre. Soft water should be used, and the temperature of the bath maintained at 75° C. Sodium carbonate may be added to the bath, but this must not exceed 2 per cent. on the weight of the goods. After scouring, the goods are rinsed in cold soft water, and for pale shades may be bleached with sodium hypochlorite (0.25° Tw.). Alternatively, the sodium hypochlorite (2.5 ml. at 50° Tw.) may be added to the soap bath, the sodium carbonate in this case being omitted. If bleached, the goods must be dechlorinated in a bath containing sodium bisulphite (0.5 to 1.0 g. per litre) for 15 min., and then washed. When dyeing acetyl rayon alone, the volume of liquor should be 20 to 30 times that of the goods, and the bath is set with 0.5 to 1.0 g. per litre of olive-oil soap in the form of a boiling solution. This can be used for dissolving the dyestuff: the boiling soap solution is poured on to the dye paste, and stirred well; the mixture is then passed through a sieve into the dye-bath. The temperature and time of dyeing depend upon the shade required, and may range between atmospheric temperature and 75° to 80° C. After dyeing, the material is rinsed in hot water (45° C.) and then in cold water. Blues and blacks may be developed with naphthol AS. A light soaping with olive-oil emulsion is recommended for knitted fabrics.

The SRA colours have no affinity for cotton, wool, or silk, and very little for other kinds of rayon. They are therefore useful for obtaining two-colour effects on unions. By choosing a suitable combination of SRA colours and direct dyestuffs, it is possible in some cases (*e.g.* with acetyl rayon and cotton) to dye either a solid shade or a two-colour effect by a single-bath process. These effects will be dealt with later.

Information on the dyeing of Nylon is given on p. 528, below.

**Azole Colours.**—Owing to the affinity which acetyl rayon has for bases, it is easy to build up azoic colours by first treating the goods with a solution of the base, and then diazotizing and coupling it with a suitable phenolic compound. The colours obtained are fast, since, after treatment with the base, the goods can be washed before coupling. Single-bath processes are used sometimes. In these the rayon is soaked in a solution containing both base and phenol, and is then treated with sodium nitrite and acid. Examples of these colours are given in Table LXIII.

TABLE LXIII.—AZOIC COLOURS FOR ACETYL RAYON.

Base.	Developer.	Colour.
Aminoazobenzene .	$\beta$ -Naphthol	Scarlet
Aminoazobenzene .	Resorcinol	Orange
Dichlorobenzidine .	$\beta$ -Naphthol	Crimson
Dianisidine .	$\beta$ -Naphthol	Purple

**Faults in Dyed Acetyl Rayon.**—The chief danger in dyeing cellulose acetate is loss of lustre due to incipient saponification. This also produces an affinity for direct dyestuffs, proportionate to the degree of saponification. Caustic alkalis should not be used in scouring processes, and sodium carbonate only in small proportions. A scouring bath has been recommended, containing per

100 gallons 2 lb. of soap and 1 to 2 pints of ammonia (sp. gr. 0.880) or 1 to 2 lb. of soda-ash. The temperature of treatment should not exceed 170° F. (76.7° C.); higher temperatures favour saponification.

### Special Effects on Rayon Goods.

Rayon goods are finished in the same manner as other knitted materials, *i.e.* steamed and pressed, care being taken to prevent mechanical damage. Previous to this they are treated sometimes to produce special effects, among which are the following:—

**Weighting.**—Rayon may be weighted with tin oxide, phosphate, or silicate in the same way as silk if a swelling agent is used also. Ammonium thiocyanate forms a suitable swelling agent. Thus the rayon is immersed in a solution of stannic chloride containing a proportion of ammonium thiocyanate chemically equivalent to the tin present. It is then washed with water to precipitate stannic hydroxide, and treated with sodium phosphate or sodium silicate. Barium sulphate produced by precipitation in the fibre may be used also.

**Delustring.**—Formerly rayon stockings were commonly delustred. Barium sulphate is suitable for this purpose. The goods are soaked in a cold solution of barium chloride, squeezed, and passed into a solution of sodium sulphate. Titanic oxide,  $TiO_2$ , gives better results. It is formed by soaking the rayon in titanous chloride solution, then treating with ammonia, and oxidizing the titanous oxide,  $Ti_2O_3$ , by exposure to air. Metallic soaps formed by precipitation give a dull finish, and emulsions of waxes such as Japan wax are very efficient.

**Waterproofing (or splash-proofing)** has been described above.

**Serrop.**—The goods are worked in a 0.5 per cent. solution of white curd soap, hydro-extracted, then treated with a 0.5 per cent. solution of tartaric acid, hydro-extracted again, and dried.

**Non-creasing rayon** is made by soaking the goods in an aqueous solution of a soluble synthetic resin, and then changing the latter into an insoluble resin by means of heat. The tensile strength and resistance to wetting also are increased by this treatment.

**Increasing Tensile Strength.**—Many processes have been suggested for this purpose. They are no longer used, however, since the strength of modern rayon is now sufficient.

## CHAPTER XXXV.

### PATTERN-DYEING AND THE DYEING OF MIXED FIBRES.

THE practical dyer must be able not only to produce a standard range of colours on the different fibres, but also to dye goods to match a particular pattern. The latter will often necessitate the identification of the class of dyestuff present in the pattern to be matched. It will also be important to know whether a single dyestuff or a mixture has been used. When the dyer has information on these points, he will often match the colour with those dyestuffs which he commonly uses, relying on his knowledge of colour-matching and the information contained in his pattern-book. The goods with which he has to deal may include those which have to be stripped and redyed, and those containing two or more different fibres. When two different fibres are present, the dyeing may include: (i) dyeing one fibre and leaving the other undyed; (ii) dyeing each fibre a different colour; and (iii) dyeing both fibres the same colour.

In the case of coloured goods it will be necessary to strip or partly strip the dyestuff before redyeing. For this purpose the following methods are available: (i) heating with a dilute solution of ammonia or sodium carbonate to remove acid or direct dyestuffs; (ii) heating with sodium hydrosulphite or decrolein in the presence of acetic acid or alkali; (iii) treatment with a dilute solution (0.5° Tw.) of bleaching powder; and (iv) heating with potassium dichromate (3 per cent.) and dilute sulphuric acid (3 per cent.). When stripping is necessary, the goods must be washed thoroughly and neutralized before dyeing. The methods used for the dyeing of mixtures of fibres may now be described briefly.

#### Cotton and Wool.

The following points are of importance in the dyeing of cotton and wool:—

- (1) Acid dyestuffs dye wool, but have little affinity for cotton.
- (2) Direct dyestuffs dye both wool and cotton in a boiling bath, but have little affinity for wool at low temperatures. Many of them will dye cotton in a cold bath.
- (3) Basic dyestuffs dye wool, but not cotton unless mordanted.
- (4) Sulphur dyestuffs dye cotton from a cold or warm bath, but leave wool undyed.
- (5) Ionamines dye wool from an acid bath, but have no affinity for cotton.
- (6) Janus dyestuffs dye both wool and cotton from an acid bath.

**Dyeing the Wool and leaving Cotton Undyed.**—For this purpose an acid dyestuff is used which is known not to stain cotton in a boiling acid bath. Sulphuric acid is replaced by acetic or formic acid to minimize the danger of tendering the cotton. After dyeing, the goods are washed with water until

free from acid. A slight stain on the cotton may be removed by careful treatment with a stripping agent.

**Dyeing the Cotton and leaving Wool Undyed.**—Either a direct or a sulphur dyestuff which will dye cotton from a cold or lukewarm bath may be used. The addition of a little Turkey-red oil assists penetration, whilst about 1 per cent. of sodium carbonate in the case of direct dyestuffs tends to keep the colour off the wool. The direct dyestuff may be diazotized and coupled or developed in the usual manner.

**Dyeing Each Fibre a Different Colour.**—This can be done in several ways:

*Dyeing the Wool First.*—In this method the wool is dyed with an acid dyestuff, and then the cotton with a direct dyestuff which does not dye wool in a lukewarm bath. The wool is dyed in the usual manner for acid dyestuffs. Complete freedom from acid is necessary before the goods are put into the direct dye-bath. Any sulphuric acid left would liberate the sulphonic acid of the direct dyestuff, and tend to make it dye the wool. This freedom from acid is ensured by first rinsing the goods, after leaving the acid dye-bath, with water, and then treating them with a weak solution of ammonia or sodium carbonate before completing the washing. For similar reasons a neutral or slightly alkaline bath is used for the direct dyestuff. The presence of alkali keeps the colour off the wool, but assists the dyeing of the cotton. Although many direct dyestuffs dye cotton from a cold or lukewarm bath, the colour is always faster if dyed at a higher temperature; but the highest it would be safe to use, if the wool is to be left undyed, is 100° F. (37·8° C.). The bath is made up with from 15 to 20 per cent. of Glauber's salt and 1 per cent. of sodium carbonate. The goods are wetted and entered into the cold bath, and the temperature is raised slowly to 100° F. (37·8° C.), dyeing being continued at this temperature for 45 min.

*Dyeing the Cotton First.*—(1) Either a direct or a sulphur dyestuff may be used which fulfils the following conditions: (a) it must dye cotton in a lukewarm bath without dyeing wool; and (b) it must be fast to boiling with an acid dyestuff in an acid bath containing Glauber's salt. The cotton is dyed, the goods are washed thoroughly, and the wool is then dyed with an acid dyestuff, together with acetic or formic acid and Glauber's salt.

(2) A mixture of a direct dyestuff and a neutral-dyeing acid dyestuff may be used, the colour of the wool being that produced by the combination of both.

(3) The cotton may be mordanted with tannic acid or Katanol in a cold bath, washed, and dyed with a basic dyestuff. The wool is then dyed with an acid dyestuff. Alternatively, the cotton may be dyed in a cold or lukewarm bath with a direct or sulphur dyestuff, and, after washing, the wool dyed with an acid dyestuff. The process may be reversed. The wool is dyed first, then washed, and treated with a cold aqueous solution of tannic acid containing 3 lb. for each 100 lb. of material. After running through this about 15 times, the goods are rinsed with water, and treated with antimony tartrate, about half as much being used as of tannic acid. They are then rinsed, and dyed in a lukewarm solution of the basic dyestuff containing 2 to 3 per cent. of acetic acid.

(4) It has been mentioned above that the ionamines dye wool from an acid bath but have no affinity for cotton. The latter could, of course, be dyed a different colour with a direct dyestuff from a cold bath.

**Dyeing Both Fibres the Same Colour.**—The methods just described for dyeing each fibre a different colour can be used to produce a solid shade on both. Either the wool or the cotton may be dyed first, and the other topped



in a second bath. Double-bath processes generally give faster colours, but are costly, and a single-bath method is preferred when it will give the required degree of fastness.

*Single-bath Process.*—Direct dyestuffs are used for this process. The goods must be quite free from acid, since this would tend to increase the affinity of the wool for the dyestuff and decrease that of the cotton. This is particularly important when goods have been treated with dichromate and acid. This treatment also increases the affinity of cotton for direct dyestuffs. As a general rule, direct dyestuffs dye wool more deeply than cotton at the boiling-point, whilst the reverse is the case at lower temperatures. Hence the shade of the mixture may be influenced by controlling the temperature of the dye-bath, and if necessary adding a little more of the dyestuff. Direct dyestuffs can be classified as (i) those giving solid shades on wool and cotton, (ii) those which dye the wool more deeply, and (iii) those which dye cotton more deeply than wool. Naturally, a member of the first class should be used if possible, but in most cases a little shading will be necessary. This can be done, as noted above, by regulating the temperature; or, in the case of wool, by the use of a little neutral-dyeing acid dyestuff. The following direct dyestuffs are suitable for the single-bath process:—

Chrysophenine G,	Chlorazol fast red F and K,
Benzopurpurine 4B,	Chlorazol black F,
Chlorazol dark green PL conc.,	Chlorazol black BXX.

Direct dyestuffs which dye cotton more deeply than wool in a boiling bath include—

Chlorazol fast yellow B and FG,	Chlorazol blue B and 3B,
Chlorazol brown LF,	Chlorazol dark blue B.

The following dye wool more deeply than cotton:—

Aurophenine O,	Brilliant dianil blue R and G,
Dianil orange N,	Dianil green GN,
Dianil red 5B,	Dianil brown 3GD,
Dianil pink BD,	Patent dianil black EB conc.

The dyestuff is dissolved, and placed in the bath, which contains from 15 to 25 gallons of water for each 10 lb. of goods and about 30 per cent. of sodium sulphate or sodium chloride. The goods are entered at 140° F. (60° C.), and dyed for 30 min. at this temperature. The temperature is then raised to the boiling-point, and dyeing continued for 45 min. If the shade is correct, the goods are removed and washed. If both wool and cotton are below the shade, a little more dyestuff is added, and dyeing continued. If the shade of the wool is correct, but that of the cotton lighter than that of the wool, the bath is allowed to cool off so that the cotton may take up the dyestuff, a little more being added if necessary. If the cotton is more deeply dyed than the wool, dyeing is continued at the boiling-point, with a little more dyestuff if necessary. If the wool cannot be brought to shade in this way, a neutral-dyeing acid dyestuff may be used.

Rudolph (*J. Soc. Chem. Ind.*, 1926, 45, B484) found that Katanol W retards the absorption of direct dyes by animal fibres, but that cotton is not affected. This fact may be utilized to facilitate the production of solid shades on unions. The wool is dyed to shade at a high temperature, the bath is then cooled to 75° to 80° C., and 3 per cent. of katanol is added. The cotton is allowed to absorb the dyestuff until the desired shade is obtained. Cotton in

half-wool materials in which the wool has been dyed with acid dyestuffs can be dyed with direct dyestuffs in the presence of katanol at 75° to 80° C.

**Dyeing with Janus Dyestuffs.**—These dyestuffs dye both wool and cotton from an acid bath. Like direct dyestuffs, some of them dye both fibres the same shade, while others dye either the wool or the cotton more deeply. The following dye both fibres the same shade:—

Janus yellow GR,	Janus brown R,
Janus red B,	Janus black I,
Janus green G.	

The dyestuff is made into a paste with acetic acid, and boiling water is then added with stirring. For light shades the bath is made up with 2 to 4 per cent. of hydrochloric acid, 2 per cent. of chromium fluoride, and the solution of the dyestuff. The goods are entered into the hot bath, and dyeing is carried out at the boiling-point, Glauber's salt being added if the wool remains too light in colour. Dark shades are dyed in a short bath with 2 per cent. of sulphuric acid. The goods are entered at 158° F. (70° C.). The temperature is raised to the boiling-point, and boiling is continued until the required shade is obtained. At the boiling-point the wool tends to be dyed more deeply than the cotton, whilst at a lower temperature the reverse is the case. Either basic or acid dyestuffs may be used for shading. Janus Brown B and Janus Grey 2B dye cotton darker than wool, while Janus Blue RG and Janus Green B give deeper shades on wool.

### Cotton and Silk.

**Leaving One Fibre Undyed.**—*Dyeing the Silk.*—Silk can be dyed, leaving the cotton undyed, by using a suitable acid dyestuff at 180° F. (82.2° C.) with about 10 per cent. of acetic acid. Glauber's salt must be used only very sparingly with silk, but from 5 to 10 per cent. is permissible. The cotton, if stained, may be cleared by careful treatment with a stripping agent.

*Dyeing the Cotton.*—The cotton may be dyed, leaving the silk undyed, by means of a direct or sulphur dyestuff in a cold bath containing a little sodium carbonate and soap. Certain direct dyestuffs can be used in this way at a temperature of 180° F. (82.2° C.). The following do not dye silk from a neutral bath:—

Chlorazol fast yellow FG,	Chlorazol fast orange D,
Chlorazol yellow GX,	Chlorazol fast eosine B,
Chlorazol fast blue 2BN.	

**Dyeing Each Fibre a Different Colour.**—The methods used are similar to those described for cotton-wool mixtures. Either fibre may be dyed first. The silk can be dyed with an acid dyestuff, using formic acid, after which the cotton is dyed with a direct dyestuff at a low temperature in the presence of alkali and soap. Alternatively, the cotton may be dyed first, and the silk afterwards with an acid or basic dyestuff. When a basic dyestuff is used, the colour of the cotton will be affected. The following is an example of a process for green and red effects on 100 lb. of goods:—

The silk is first dyed with 4 lb. of Quinoline Yellow and 1 lb. of Light Green SF yellow shade in the presence of acetic acid. The goods are entered into the lukewarm bath, and the temperature is raised to 140° F. (60° C.) and then to 175° F. (79.4° C.), acetic acid being added till the bath is exhausted sufficiently.

Dyeing is then finished by raising the temperature once or twice to the boiling-point. After rinsing, the goods are mordanted with 10 lb. of tannic acid in a cold bath, a little hydrochloric acid being added to the bath. The tannic acid is fixed with 4 lb. of antimony tartrate. The mordanted goods are then dyed in a cold bath with 1 lb. of Safranin XX and 1 lb. of Auramine II in the presence of acetic acid. If the cotton becomes stained while the silk is being dyed, it can be cleared by means of a weak bleaching-powder solution, followed by souring and rinsing.

Two-colour effects may be produced also, as with wool and cotton, by using a mixture of an acid dyestuff, which dyes silk from a neutral bath, and a suitable direct colour.

**Dyeing Both Fibres the Same Colour.**—Certain direct dyestuffs dye silk and cotton nearly the same shade, whilst others dye either the silk or the cotton more deeply. Shading may be effected by means of a basic dyestuff in a fresh bath. The katanol method mentioned above can be used. The silk may be dyed first with an acid dyestuff, and the cotton matched with a direct or sulphur dyestuff in a cold or lukewarm bath.

It may be noted that some direct dyestuffs, whilst dyeing cotton and silk to apparently the same depth, yield shades of differing tone, so that it may be necessary to correct these with neutral-dyeing acid dyestuffs or other direct dyestuffs. Dyestuffs which give solid shades individually do not always do so in combination. For current hosiery shades, Chlorazol Brown G, Chlorazol Green BN, and Chlorazol Fast Red 10B form a satisfactory combination, a little Chlorazol Yellow GX being used to shade the cotton. Another combination is Chlorazol Fast Red FG, Chlorazol Fast Yellow B, and Chlorazol Fast Black BK. Chlorazol Brown LF gives fawn and brown shades, but the cotton may require a little Chlorazol Yellow GX. Flesh tints may be obtained with Chlorazol Fast Red K and Chlorazol Fast Orange AG.

### Silk and Wool.

In this case the problem is complicated somewhat by the fact that both fibres have similar dyeing properties, except that the temperature factor varies. Silk can be dyed with both acid and basic dyestuffs in a cold or lukewarm bath, leaving the wool undyed. On the other hand, many acid dyestuffs, as noted above, do not dye silk in a boiling bath in the presence of about 10 per cent. of acetic acid. Direct dyestuffs also can be selected which dye both fibres alike at 185° F. (85° C.), or which, in the presence of sodium carbonate, have a greater affinity for one fibre or the other. The following are examples of the methods used:—

**Dyeing the Wool and Leaving the Silk Undyed.**—An acid dyestuff is used with from 10 to 20 per cent. of acetic acid at about 185° F. (85° C.) or at the boiling-point. The dyestuff may be added in one or several portions. The following is an example:—

The dye-bath is made up with about 5 per cent. of the dyestuff (*e.g.* acid magenta) and 10 per cent. of acetic acid. The goods are wetted and entered at about 185° F. (85° C.). The temperature is raised to very nearly the boiling-point, and dyeing continued for from half an hour to an hour, 2 per cent. of acetic acid being added every 10 or 15 min. up to a maximum of 20 per cent.

The silk will generally be stained; if so, the dyestuff is removed from it by stripping with ammonium acetate. The dyed goods are worked for 10 min. in a boiling bath containing about 3 per cent. of neutralized ammonium acetate, being removed as soon as the silk is clear. Prolonged treatment

must be avoided, since some of the colour is stripped from the wool also. This is avoided by treating the goods twice for 5 min. in fresh baths containing half the quantity of ammonium acetate. Other methods of clearing the silk may be employed, viz.:—

(1) When the silk is only slightly stained, a bran bath is suitable. One pound of bran is mixed with 10 gallons of lukewarm water, and the goods are worked in it for about 20 min., then washed, and brightened with dilute acetic acid.

(2) Sometimes a warm bath of water and Turkey-red oil will clear the silk.

(3) Other dyestuffs, such as magenta and tartrazine, are best cleared by means of a very dilute bath of hydrogen peroxide. The silk having been cleared, it may be left white or dyed as required.

Examples of acid dyestuffs which do not dye silk in a boiling acid bath are tartrazine, acid magenta, and indigo carmine.

**Dyeing the Silk and Leaving the Wool Undyed.**—Basic dyestuffs may be employed which have little affinity for wool at a low temperature. The dye-bath should contain about 5 per cent. of acetic acid, as this tends to keep the colour off the wool. The goods are entered cold, and the temperature may be raised gradually to a maximum of about 86° F. (30° C.).

Suitable basic dyes for the silk include auramine, safranine, rhodamine, malachite green, and methylene blue.

**Dyeing Each Fibre a Different Colour.**—Two-bath processes may be employed; for example: The wool is dyed as described above, and the silk cleared if necessary with ammonium acetate. The silk may then be dyed with a suitable basic dyestuff as described in the previous section. Or, alternatively, it may be treated in a lukewarm bath with a suitable direct dyestuff which is not taken up by the wool. Two-colour effects can be obtained also by a single-bath process, by using combinations of dyestuffs which dye both wool and silk under the conditions of the dye-bath, together with others which only stain the silk or leave it undyed. For example, Wool Green S dyes both silk and wool from a boiling acid bath, but Acid Magenta and Azoflavine are taken up by the wool only. Hence, with a mixture of these three colours, the silk will be dyed green and the wool a dark olive colour.

**Dyeing Both Fibres the Same Colour.**—This is not very easy. Although wool and silk have the same affinity for dyestuffs, yet a particular colour does not always act in the same way with both. Thus the acid dyestuffs, as a rule, dye wool more deeply than silk from a boiling bath, and the silk more deeply at lower temperatures. They may be classified according to whether they (i) dye both fibres alike; (ii) dye the wool from an acid bath, only staining the silk or leaving it undyed; or (iii) dye the silk chiefly at moderate temperatures.

**Dyeing with Acid Dyestuffs.**—Only those which give a solid shade on both fibres should be used. The following are examples of methods:—

(a) The bath is made up with the dyestuff, 1 to 3 per cent. of acetic acid, and 5 to 10 per cent. of Glauber's salt. The material is entered at about 160° F. (71.1° C.), and the temperature raised to the boiling-point for an hour. If the silk is not dyed sufficiently, it may be shaded by cooling off the bath and adding a little more of the dyestuff.

(b) The dyeing is started in a cold bath made up as above, but with only about three-fifths of the quantity of dyestuff to be used. The temperature is raised to the boiling-point in about half an hour, and the bath kept at the boiling-point until the wool has acquired the desired shade. The bath is then cooled to 140° F. (60° C.), and the remainder of the dyestuff added, or sufficient

of it to bring the silk up to the same shade as the wool. The silk may be shaded also by means of a basic dyestuff added to the cooled-off bath.

**Dyeing with Direct Dyestuffs.**—There are many direct dyes which dye mixtures of wool and silk a solid shade, and provide the easiest method of dyeing mixtures of these fibres. It must be remembered that while, as a rule, wool develops its maximum affinity at the boiling-point, silk has rather a lower affinity at this temperature than at lower ones. It can be dyed at temperatures ranging from 140° F. (60° C.) to the boiling-point. Mixtures of wool and silk are dyed for an hour in a boiling neutral bath. If the wool is more deeply dyed than the silk, the bath may be cooled to 140° F. (60° C.), more dyestuff being added if necessary. If the wool has too light a shade, either the boiling may be continued with a little more dyestuff, or some acetic acid (1 to 2 per cent.) may be added to the bath, and the boiling continued. Acid, as noted before, tends to make the wool dye more deeply.

The following list gives some details of I.C.I. dyestuffs with reference to the dyeing of mixed fabrics:—

(1) *Acid Colours.*

(a) *Dyeing wool and silk alike :*

Citronine Y conc. and R conc.,	Fast red EAS (both solid shade),
Metanil yellow Y,	Bordeaux B,
Milling scarlet 5B,	Acid green G,
Coomassie scarlet,	Lissamine green B,
Cardinal red J (both solid shade),	Disulphine blue A.

(b) *Leaving silk undyed :*

Acid yellow 29210 (unstained),	Indigo carmine X (tinted),
Orange 2G (slightly tinted),	Durasol acid blue B (unstained),
Azogermanine B (tinted),	Fast acid blue RH (unstained).
Lissamine violet 2R (tinted),	

(2) *Direct Colours.*

(a) *Dyeing cotton in cold bath, but with little or no affinity for wool or silk :*

Titan yellow G,	Chlorazol violet R,
Chlorazol yellow GX,	Chlorazol sky-blue FF,
Chlorazol fast pink BK,	Brilliant black BXX.

(b) *Dyeing solid shades on wool, silk, and cotton :*

Benzopurpurine 4B,	Chlorazol black BXX,
Chrysophenine G,	Chlorazol fast red F and K.

(c) *Dyeing wool and cotton the same shade :*

Chlorazol dark green PL conc.

(d) *Dyeing cotton darker than wool :*

Chlorazol fast yellow B and FG,	Chlorazol black BH.
Chlorazol dark blue B,	

(3) *Acid Colours.*

*Suitable for shading in a neutral bath :*

Acid orange IV,	Cardinal red J,
Coomassie navy blue,	Fast red EAS.

### Mixtures containing Regenerated Cellulose.

Rayons consisting of regenerated cellulose have similar dyeing properties to those of cotton, which have been described already. In the case of viscose, the difference between high- and low-number direct dyestuffs must not be forgotten. The dyeing of hose and half-hose is complicated by the uneven distribution of the rayon. The heel, welt, and toe consist often entirely of cotton, the rayon being confined to the panel.

**Silk and Rayon.**—The methods of dyeing these mixtures are practically the same as those described for silk and cotton. To leave the rayon undyed, an acid dyestuff is used in the presence of acetic acid and very little Glauber's salt. Dyeing is begun at about 100° F. (37·8° C.), the maximum temperature being 180° F. (82·2° C.). In order to dye each fibre a different colour, the silk can be dyed first with an acid dyestuff which does not stain regenerated cellulose, and the rayon then dyed with a direct dyestuff in a cold or lukewarm bath containing sodium carbonate and soap or Turkey-red oil. Two-colour effects on these mixtures are not common, the principal requirement being a solid colour on both fibres. For this purpose direct dyestuffs are generally used, the temperature of the dye-bath being kept at 180° F. (82·2° C.), since many direct dyestuffs do not dye silk at the boiling-point.

**Wool and Rayon.**—The methods used for these mixtures differ from those for silk and rayon only in that the wool may be dyed at the boiling-point. Two-colour effects can be dyed by a single-bath process using both acid and basic dyestuffs. It was shown by Trotman and Bateman (*J. Soc. Dyers Col.*, 1931, 47, 231) that if the reaction of a dye-bath is more acid than pH 5·5, basic and acid dyestuffs do not react with each other. The affinity of wool for basic dyestuffs is very small at low temperatures; on the other hand, that of regenerated celluloses such as viscose is quite marked. The dye-bath is made up with the selected acid dyestuff, 10 per cent. of Glauber's salt, and 1·5 per cent. of tartaric acid per litre of liquor. The fabric is introduced at 40° C., and the temperature raised to 80° C. and kept at this value until the wool is dyed to shade. The bath is then cooled to 60° C., and the solution of the basic dyestuff added, little by little. The following dyestuffs are suitable:—

#### (a) Acid dyestuffs:

Suprazol brilliant red B,  
Fast acid violet 2 RN,

Brilliant geranine B,  
Alizarine direct grey,

Azorubinole,

and others.

#### (b) Basic dyestuffs:

Rhodamine 3B,  
Brilliant phosphine G,  
Malachite green,

Chrysoidine R,  
Methylene blue,  
Methyl violet,

and others.

Direct dyestuffs are used generally for dyeing both fibres the same colour.

### Mixtures containing Cellulose Acetate.

**Acetyl Rayon and Cotton, Wool, or Silk.**—Acetyl threads may be left undyed by using a direct dyestuff which has no affinity for the rayon. In the

case of wool or silk, acid dyestuffs would be available also. Direct dyestuffs with no affinity for acetyl rayon include the following chlorazol colours:—

Chlorazol yellow GX,  
Chlorazol fast yellow B and  
BN conc.,  
Chlorazol orange AG,  
Chlorazol brown PB,  
Chlorazol red K,

Chlorazol pink BK,  
Chlorazol scarlet 4BS,  
Chlorazol violet R,  
Chlorazol sky-blue FF and GW,  
Chlorazol black BH and GF.

For cotton and acetyl rayon a sulphur dyestuff in a cold bath may be used, provided precautions are taken to prevent saponification of the esterified fibre (see below). The cotton may be dyed also with a vat dyestuff. Messrs. British Celanese Ltd. have patented the use of sodium phenate for protecting the cellulose acetate against saponification. Since phenol is a very weak acid, its sodium salt will act as a weak alkali towards the reduced vat dyestuff, but the danger of saponifying the cellulose acetate will be reduced to a minimum. The vat is prepared as follows: 100 g. of the vat colour are made into a paste with a little Turkey-red oil, and 10 litres of water are added at such a temperature as will give a final temperature of 50° C. Three kilograms of sodium phenate are added, after which 300 g. of sodium hydrosulphite powder are sieved in, and the mixture is then stirred until the vat colour is completely reduced. This preparation forms the stock vat. The dye-bath is made up with 20 times as much water (by weight) as goods. To this is added sufficient sodium phenate to give a concentration of 0.6 g. per litre, sodium hydrosulphite to give 1.5 g. per litre, and glue to give 0.35 g. per litre, together with an appropriate volume of the stock vat. The goods are entered and dyed at a temperature of from 40° to 60° C. After dyeing, they are squeezed, oxidized, rinsed with soft water containing 0.2 g. per litre of sodium hydrosulphite, and finally rinsed well with soft water. After the cotton has been dyed, the celanese also may be dyed, by SRA or other suitable colours, thus producing solid or two-colour effects. The same results may be obtained in a single bath by choosing suitable mixtures of SRA colours and direct dyestuffs.

The Ionamines are used for dyeing mixtures of cellulose acetate and cellulose. Since cotton and other forms of cellulose have no affinity for ionamines, whilst acetyl rayon has no affinity for certain direct dyestuffs, mixtures of the two fibres may be dyed in two colours by a suitable mixture of ionamines and direct dyestuffs. The colour on the cotton may be diazotized and developed after dyeing.

**Acetyl Rayon and Wool or Silk.**—When both fibres are to be dyed the same colour, either a single- or two-bath process may be used. In the latter case, the rayon is dyed first with a suitable SRA colour or other similar dyestuff, the goods are rinsed well, and the wool or silk dyed with an acid dyestuff in a bath containing Glauber's salt and formic acid. For a single-bath process, mixtures of acetate-dyeing dyestuffs together with neutral-dyeing acid dyestuffs are employed; the dye-bath should contain 10 per cent. of Glauber's salt. The dyeing is started cold, and the temperature raised to 85° C. in two hours. The following neutral-dyeing acid dyestuffs are recommended as having no affinity for acetyl rayon:—

Coomassie navy-blue 2RNX,  
Coomassie milling scarlet G,  
Quinoline yellow extra,  
Patent blue 9879,  
Brilliant milling violet 84B,

Diphenyl fast grey B conc.,  
Diphenyl fast brown GN extra,  
Diphenyl chlorine yellow FF,  
Chrysophenine G,  
Rhodamine B.

## CHAPTER XXXVI.

### THEORY OF COLOUR AND COLOUR-MATCHING.

THE colour of an object is not one of its intrinsic properties. It has no real existence apart from the observer, but is a manifestation of the light which the object absorbs, transmits, and reflects according to its physical state. Light consists of electromagnetic vibrations or waves which have frequencies lying between certain narrow limits. These waves are transverse, *i.e.* the direction of propagation is perpendicular to the plane of vibration, and they travel through space at the rate of 186,772 miles per second. The impact of these waves upon the retina of the eye causes the sensation of light; and the colour

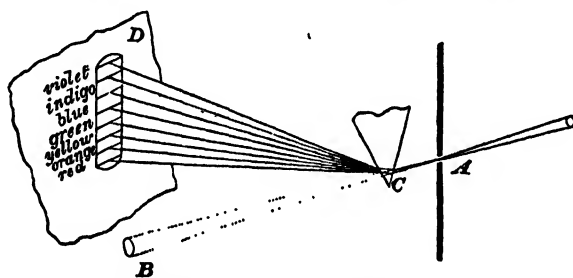


Fig. 189.—Dispersion of White Light.

depends on the frequency of the impacts, or the wavelength of the impinging light.

White light, or sunlight, is composed of rays of various wavelengths or frequencies, each corresponding to a different colour sensation. This was discovered by Newton. If sunlight is allowed to enter a dark room through a small aperture *A* (Fig. 189) in a shutter, the beam, when falling perpendicularly on a screen, will form a clear, bright, circular spot at *B*. If, now, a prism *C* is interposed in the path of the beam near the aperture, with its refracting edge parallel to the slit, the light will be refracted towards the base of the prism. The patch on the screen will no longer be white, nor circular, but separated into a number of differently coloured patches *D* corresponding to the colours of the rainbow. This is termed the *solar spectrum*. The different colours pass imperceptibly one into another. The rays which have undergone least deviation produce red light; those which have been deviated most, violet. Between the red and the violet come the other colours of the spectrum, in the order indicated in the illustration. The red rays are those having the longest wavelength and the lowest frequency, the wavelength decreasing and the frequency increasing towards the violet end of the spectrum. Wavelengths in the visible region are generally expressed in Ångström units, or angstroms



(1  $\text{\AA}$ . =  $10^{-10}$  m. =  $10^{-8}$  cm.) or in millimicrons ( $1\text{m}\mu$ . =  $10^{-6}$  m. =  $10^{-7}$  cm.). A millimicron is sometimes denoted by the Greek letter  $\lambda$ .

The more exact investigation of the nature of the light emitted by any object is made by means of a spectroscope (see Fig. 190). This consists of a prism or set of prisms, a *collimator* or tube fitted with a convex lens, and a telescope. The convex lens is fixed in the collimator between the prism and the slit at the distance of its principal focal length from the latter. The effect of this is that the rays from any point of the slit emerge from the collimator parallel, as if they came from a much larger slit (the virtual image of the real slit) at a much greater distance. The prism is set at its minimum deviation,

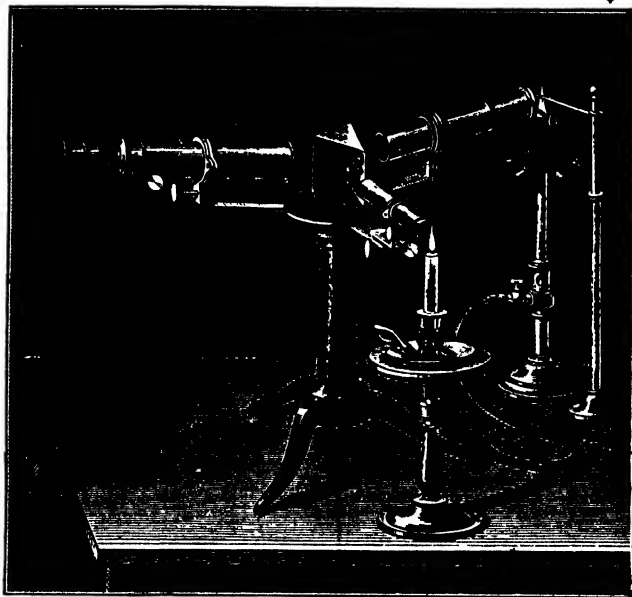


Fig. 190.—Spectroscope.

and forms a virtual image of the first virtual image at the same distance from the prism, but in a different direction. The telescope is used to view this second virtual image. In Fig. 190, the collimator is the farther tube, the lens being at the end of the tube next to the prism, while at the far end, close to the flame, is a slit consisting of an opening between two parallel knife-edges, one of which can be moved by means of a screw. The near tube with a candle contains a scale, which is seen by the observer through the telescope. The position of any particular part of the observed spectrum can thus be fixed.

When the spectrum of sunlight is examined with the spectroscope, certain gaps or dark lines are observed at fixed points on the scale. These are termed *Fraunhofer lines*, and the more important are designated by letters of the alphabet. They indicate that light of a particular wavelength, or refrangibility, is either absent or has been absorbed by the atmosphere of the sun. Since their position is fixed, and they are easily recognized, they are of use as points of reference.

The red light-waves have a frequency of 392.4 billions ( $10^{12}$ ) per second.

Passing from the red to the violet end of the spectrum, the frequency increases gradually to 740·5 billions per second. Between the red and violet ends are also all the other colours of the rainbow (not white and black), among which we can distinguish definitely red, orange-red, orange, orange-yellow, yellow, green, greenish-blue, blue, bluish-violet, and violet. The eye cannot perceive light with a frequency of less than 392·4 or more than 740·5 billions per second, although waves outside these limits are present in ordinary sunlight. The frequencies corresponding to these common colours are—

	Billions.		Billions.
Red . . . . .	392·4	Greenish-blue . . . . .	591·4
Orange-red . . . . .	484·1	Cyan-blue . . . . .	606·0
Orange . . . . .	503·3	Blue . . . . .	635·2
Orange-yellow . . . . .	511·2	Bluish-violet . . . . .	685·8
Yellow . . . . .	517·5	Puce violet . . . . .	740·5
Green . . . . .	570·0		

Beyond the violet end of the spectrum are the *ultra-violet*, and beyond the red the *infra-red* rays. The former are active in inducing chemical reactions, and the latter are heat rays. Neither are visible to the eye.

The colour of an object is due to its absorption of all the colours of the spectrum except those corresponding to its true colour; these are reflected, and enter the eye. But the apparent colour of an object depends, also, upon the nature and quantity of the light with which it is illuminated, *i.e.* (i) on the wavelengths of the particular rays which, either alone or in excess of other rays, are falling on a given area of the retina; (ii) on the amount of coloured light falling on the area in a given time; and (iii) on the amount of white light falling on the area in the same time. The first determines what is called the *hue*, the second the intensity, and the third the amount of saturation.

When all the colours of the spectrum are recombined, white light is again produced. When ordinary white light strikes the retina of the eye it is not perceived as a mixture of the colours of the spectrum, but is translated into the sensation of white light.

Similarly, when light from a coloured object is received, the constituent lights are combined by the eye, and we perceive the resulting compound colour. But the retina of the eye is not constructed to receive and perceive light of every possible wavelength or frequency. It can perceive only certain of them, which we call primary colours. The retina contains the ends of nerves, some of which transmit impulses corresponding to each of these primary colours to the brain, where they are combined to give the resulting colour. The primary colour sensations correspond to either (i) red, yellow, and blue; or (ii) red, green, and violet. When all the nerve-ends of the retina are stimulated equally, we get the impression of white light. If only those which are sensitive to, say, red and blue are stimulated, the colour is perceived as a compound one depending upon which set of nerve-ends receives the greater stimulation.

**Complementary Colours.**—In order to produce in the eye the sensation corresponding to white light, it is not necessary to recombine all the colours of the spectrum. White light may be produced also by mixing light of two colours. Thus, if the red of the spectrum is mixed with successive parts of the rest of the spectrum, it will be found that when it is combined with a particular part of the green or blue-green, white light is obtained. These two colours are said to be *complementary* to each other. The pairs of complementary colours in Table LXIV are given by Foster (*Text Book of Physiology*, 3, 1229). There are also other complementary colours: in fact, every colour of the spectrum

from red to greenish-yellow has its complement on the blue side of the spectrum. The complementary colour of greenish-yellow is violet, which is the limit of the visible spectrum.

TABLE LXIV.—COMPLEMENTARY COLOURS.

Colour.	Wavelength, m $\mu$ .	Colour.	Wavelength, m $\mu$ .
Red . . . . .	656	blue-green	492
Orange . . . . .	608	blue	490
Gold-yellow . . . . .	574	blue	482
Yellow . . . . .	564	indigo-blue	462
Greenish-yellow . . . . .	564	violet	433

— Every colour can be made by mixing together the proper proportions of the three primary colours, together with black and white. Black is simply the negation of colour, an object appearing black when it absorbs all the light which falls on it and reflects none. Grey is a white of low intensity, or white mixed with black. When the primary colours are mixed, the intermediate colours of the spectrum are obtained, these being called *secondary colours*; thus:

Red and yellow give orange.

Yellow and blue give green.

Blue and red give violet.

It has been stated above that when lights of complementary colour are mixed, white light results. The term *complementary* is used also in a somewhat different sense. If an orange dyestuff, produced by mixing red and yellow, is mixed with the same quantity of its complementary colour, blue, a black is produced, because all the light which falls on the mixture is absorbed. Similarly, yellow and indigo-blue, or any other pair of the complementary colours given in Table LXIV, will give black, or, if in sufficiently dilute solution, grey, i.e. a mixture of black and white. If one colour is in excess, it is softened or toned down by the addition of small quantities of the other two. The effect of mixing black with other colours is as follows:—

Yellow and black give brown.

Green and black give olive.

Red and black give red-brown.

Blue and black give grey-blue.

In Table LXIV, yellow and blue are said to be *complementary*, i.e. they produce white light when combined. But if yellow and blue paints are mixed, the resulting mixture is green. In the same way, a fabric dyed with a mixture of yellow and blue dyestuffs may be dyed green. The light from the yellow pigment and that from the blue pigment both contain green. But blue and yellow, being complementary, produce white light, and hence the eye perceives only green light mixed with white. The colour of a solid substance is determined by the light which is reflected from it to the eye of the observer. Solid substances both absorb and reflect light. If light of all frequencies is

reflected, the colour of the object appears white, while if no light is reflected it will be black. Black and white together give grey. Thus, the colour of an object is due to the fact that it absorbs all the different coloured lights in ordinary sunlight, except those which correspond to its colour, and which are reflected from it. This is why a coloured body may have different apparent colours in daylight and artificial light. Thus, a red substance absorbs all the various coloured lights except red, which it reflects, and if it is illuminated by white light, exhibits its true colour; but if it is illuminated by yellow light containing no red, there is nothing which it can reflect, and hence it appears to be black. The same thing would happen if it were illuminated with white light composed of the complementary colours yellow and blue. In artificial light, yellows, greens, and blues frequently appear differently from in daylight, and two colours which may match each other in daylight do not do so at night.

The colour of transparent objects is due to selective absorption of certain rays and transmission of the rest. But it depends also upon the thickness. In thick layers or in a concentrated solution, a substance may absorb completely certain rays which in a thin layer would be transmitted. Solutions of dyestuffs act in a similar manner, selecting and absorbing certain of the light rays and allowing the others to pass through. In the case of textile fibres the unabsorbed light is chiefly reflected, and not transmitted. Thus, in a general way, a dyed fabric acts like a solution of the dyestuffs which it contains. Some dyestuffs are *dichroic*. Thus magenta and eosine, for example, give, when dyed, different colours from those of the solid dyes, due to the fact that the proportions of the rays absorbed and reflected from thin and thick layers are not the same. Occasionally dyestuffs may be *fluorescent*, i.e. have the power of increasing the wavelength of the light which they transmit; fluorescein and eosine are examples. In this way the ultra-violet rays of the spectrum may be rendered visible.

In dealing with dyed materials there are other factors to be considered besides the actual colour. One of these is *intensity*. A white object is one which reflects light of all frequencies; a black object absorbs all and reflects none; while a grey object both absorbs and reflects all colours. The shade or tone of a particular colour is affected by the amount of white light which it reflects, or by the proportion which it absorbs, i.e. upon the presence of either grey or black.

**Colour-matching.**—Although, theoretically, every colour can be matched by using suitable proportions of the three primary colours, red, yellow, and blue, yet when using dyestuffs this is not always possible, and hence the secondary colours are employed as well.

Artificial dyestuffs are not pure colours, i.e. they do not emit rays of a uniform wavelength, but in practically all cases rays of differing colours. The yellows may have a red or green tone, the olives may be mixed with green or red, the reds with yellow or blue. The composition of the rays can be seen by observing the *absorption spectrum* of the dyestuff. When white light is passed through a solution of a dyestuff, and the transmitted rays are examined by means of a spectroscope, they are separated into their component colours. Every dyestuff gives a characteristic absorption spectrum, and upon this depends largely its behaviour when mixed with other colours. Thus, Indigo Carmine give an absorption spectrum which shows a dark band in the yellow, but all the other rays pass through, thus producing a blue mixed with white light. This transmitted white light gives a colour its brilliancy. The absorption spectrum of a dyestuff may be observed by passing white light through a

dilute solution contained in a cell placed in front of the spectroscope slit; a microspectroscope is also suitable, or a direct-vision spectroscope.

In dyeing to pattern, a single dyestuff would be used if possible. But if no single dyestuff will give the result desired, mixtures must be employed. Perhaps the addition of a small quantity of a second dyestuff towards the end of the dyeing will be sufficient to produce the exact tint required. When using compound colours, only those with similar dyeing properties can be used together. One could not, for example, dye with a mixture of a direct and a basic dyestuff, though the latter can be used for topping the former to match off the exact shade. Again, when two or more dyestuffs are used together in the same bath, they should have similar powers of exhaustion, and should not be dichroic. Fastness and cost must also be considered.

The fact that dyestuffs are not homogeneous makes it impossible to match colours with the three primary colours alone. The secondary colours, orange, green, and violet, must often be made use of as well. The following examples (*Dyer and Calico Printer*, 1924, 128) will illustrate this: If a red of a bluish shade or tone is combined with a blue of a greenish tone, the result is not a true violet; but if a blue of a red shade were used, a true violet would be produced. This is because the blue tone of the red mixed with the red tone of the blue gives a violet tone to the violet, or, in other words, gives a full-toned violet. The same principle is applicable to the other primary colours, and the results are given in tabular form below, where R, B, and Y indicate red, blue, and yellow tones respectively:

Blue (R) and red (B)	.	.	.	.	Violet
Blue (Y) and yellow (B)	.	.	.	.	Green
Yellow (R) and red (Y)	.	.	.	.	Orange
Yellow (B) and blue (Y)	.	.	.	.	Green
Red (B) and blue (R)	.	.	.	.	Violet
Red (Y) and yellow (R)	.	.	.	.	Orange

The tone of a colour may be changed without changing the colour itself, as is illustrated in the following table:

Blue (Y) and violet	.	.	.	.	Blue (R)
Blue (R) and green	.	.	.	.	Blue (Y)
Red (B) and orange	.	.	.	.	Red (Y)
Red (Y) and violet	.	.	.	.	Red (B)
Yellow (B) and orange	.	.	.	.	Yellow (R)
Yellow (R) and green	.	.	.	.	Yellow (B)

Suppose, for example, that it is desired to convert a blue of a greenish tone into a good navy-blue. A navy-blue is generally a red shade of blue. If, however, the blue with a greenish tint were topped with a little red, the green and the red would combine, since they are complementary colours, and the shade would become flat. But if a violet with a bluish shade were used, the blue would be increased, and at the same time the red in the violet would neutralize the green tone of the original colour. If there is too much red in the bath, green will tone it down or *kill* it; if too much yellow, violet must be used; and if too much blue, orange is required.

Similarly, a black with a bluish tint may be rendered blacker by the addition of a little yellow dye. Thus, logwood is generally dyed together with some fustic. Speaking generally, shades are made lighter by increasing the amount of white light reflected, while admixture of grey or black may either alter the shade or produce a different colour. The effect of black is given above. Black

or grey is used for altering the intensity of a colour (or its luminosity), while red and orange make a shade brighter without altering its colour. When matching a given colour, its composition in terms of primary colours and grey may be ascertained by some form of tintometer or colour-analyser, or a knowledge of the effects produced by admixture of one primary colour with another may be relied on.

*Lovibond's tintometer* (Fig. 191) can be made use of for determining the composition of the colour of a dyestuff. It consists of an apparatus which cuts off side light, and gives a direct view of the solid or liquid whose colour is to be estimated; the sample, placed in a standard cell in the case of a liquid, occupies one-half of the field of view. The colour is then matched by a series of standard glasses of various tints of the three primary colours, red, yellow, and blue. The apparatus can be used with reflected light, as shown in the diagram, or, if placed horizontally, with direct transmitted light. A north light should be used. The liquid to be tested is placed in a  $\frac{1}{2}$ -inch or 1-inch cell at the end of the left-hand compartment, and the standard glasses are adjusted in the right-hand compartment until the two colours exactly match when viewed through the eyepiece. The standards are arbitrary but rigidly fixed, the unit of each colour being derived from a definite, pure, chemical compound, which can be reproduced with exactness. The results obtained are tabulated according to the visual sensations they produce. This is illustrated by the following example:—

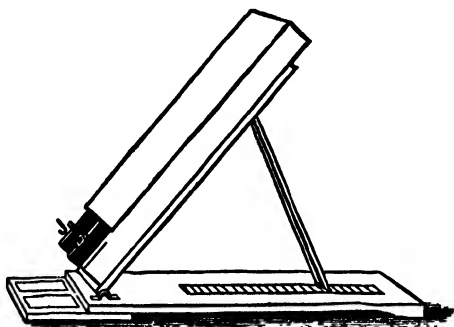


Fig. 191.—Lovibond's Tintometer.

The glasses used were red, 2·7; yellow, 0·5; and blue, 1·5. Now 0·5 unit of red, yellow, and blue will, if superimposed, give 0·5 unit of black. Hence, we have this quantity of black as a component of the colour. There are left 1·0 unit of blue and 2·2 units of red; but 1·0 of blue, together with 1·0 of red, gives 1·0 of orange, leaving 1·2 of free red. Hence the visual composition is black, 0·5; orange, 1·0; red, 1·2.

The analysis of the colour of a dyed fabric can also be made with the Bolton and Williams colorimeter, which has been described in Chapter III.

**Colour-matching by Synthesis.**—The analytical resolution of a colour into the proportions of its primary constituents can give a dyer only a limited amount of information upon which to base constructive experiments. The principles of matching a colour by synthetic methods, using the primary colours and grey, are in themselves simple, but in practice demand great experience. Starting with red, the introduction of yellow gives various shades of orange; and of blue, violet-blues to violet. Yellow mixed with blue produces green; while red, yellow, and blue together give grey or black. Thus from the primary colours we obtain certain secondary colours: orange, green, and violet. The shade of these compound colours depends upon the proportions of the primary constituents, and also upon their tone and purity. If there were only one red, yellow, or blue dyestuff available, the dyer could rely upon the results of the colour analysis. But there are numerous reds, blues, and yellows, and although two red dyestuffs may appear to be alike,

yet they may not give the same results in dyeing. For two dyestuffs to give identical results, they must absorb and transmit or reflect exactly the same kinds of light—that is, they must have the same absorption spectra. If the spectra are different, they may not give the same colours when illuminated by sunlight and artificial light, and they may also act abnormally when mixed with other dyes.

A dyer does not necessarily use both primary and secondary colours in matching. Many employ only orange in addition to yellow, red, and blue. The following may be taken as examples of the principles adopted in producing some common shades, though, naturally, different dyers would not use the same methods:—

*Greys* may be produced by dyeing black in light shades. But many dyers prefer to use the primary colours, since in this way more body is obtained. In mixing a grey, the main colour is blue, combined with red, orange, and yellow. Orange may, of course, be omitted, since red and yellow produce the same effect, but it is very generally used with the primary colours. The first mixing may be either too thin, too red, or too blue. In the first case, a little more of each of the colours used may be added in the original proportions. If the shade is too red, it can be corrected by adding a little blue together with yellow. If the shade is bluish, this can be neutralized by means of orange. If the original shade is too heavy, the only thing to do is to dilute the liquor. It is always better to obtain too light a shade at first, rather than, in the hope of hitting it off at once, to get too heavy a colour. There are very many different greys obtainable by varying the proportions of the constituent colours. Thus, mole grey contains a relatively large proportion of blue, while in silver grey there is less blue and relatively more orange. Browns are mixed in a similar manner, but larger proportions of red and orange are used, and only sufficient blue and yellow to neutralize partly the effect of the red. If the colour is too red, blue and a little yellow are added. A greyish tone indicates that too much blue has been used, and orange or red must be added. Orange tends to give brighter, and red duller shades, and these effects must be allowed for.

Other colours are usually easier to obtain, and their constituents more obvious. Thus, *green* is simply blue mixed with yellow, the particular shade depending on the proportions used. The addition of red gives it a greyer tone, since it combines with some of the yellow and blue to make black. Orange has a somewhat similar effect.

The *reds*, again, are fairly easy to match. Bright red, or flame red, which approaches orange, can be made by mixing red with yellow or orange. On the other hand, the introduction of blue tends to produce purple, and a bluish purple can be made redder by the introduction of either red, orange, or even yellow.

For *blues* it is desirable to have a light colour for shades such as sky-blue, and a deep blue for darker colours, such as royal blue. Intermediate shades can be obtained by mixing the two. Navy-blue is readily obtainable without mixing.

*Blacks* again, like navy-blues, are constantly required, and it is always better to use a black dyestuff than to compound the colour from red, yellow, and blue.

It has been mentioned already that the colour of an object is influenced by the light which illuminates it. Matching of colours should be carried out in daylight if possible, and a north light is the best to use. Gaslight and some kinds of electric light are rich in red and yellow rays, and comparatively poor in those from the violet end of the spectrum. Colours which reflect or transmit

these last rays will, therefore, be affected by this deficiency, especially if at the same time they transmit also red rays. Thus, a fabric which appears blue by daylight may become red when viewed by artificial light, the shade varying with the proportion of blue and violet light the latter contains. If matching is carried out by means of artificial light, the supply should contain all the colours of the spectrum, in approximately the same proportions as ordinary daylight. This can be secured by using the "Daylite" lamp, which cuts out by a special screen the excess of red and violet rays produced by an electric arc. The "Sherringham daylight lamp" is also suitable for this purpose.

It is to be noted that dyed goods appear darker when wet than dry. An experienced dyer allows for this, but it is safer for others to dry a sample before matching. Further, one should not look at the sample too long before judging, since the eye quickly becomes tired, and unable to appreciate small differences in shade.

While scientific analysis helps in dyeing compound colours, knowledge of the particular dyestuffs used, experience, and a good eye for colour are the most important factors. Hence a practical dyer limits the number of dyestuffs used as much as possible, and works out a set of standard formulæ with a few which he knows thoroughly. But he should ensure that the quality of his standard colours remains constant. The introduction of one with a different absorption spectrum may necessitate the alteration of every formula.

Finally, the methodical dyer keeps a written record of the weights of the different colours which he has used in matching every new colour or shade, together with a sample of the dyed fabric. The importance of this cannot be too strongly emphasized. These records and patterns are very helpful in reproducing shades which have been dyed before, and often serve as a guide in the production of new colours. The dyeing of a new colour or shade can frequently be accomplished by finding the nearest approach to it in the pattern book, and using this as a starting-point.



## CHAPTER XXXVII.

### THE IDENTIFICATION OF DYESTUFFS ON DYED GOODS.

THE identification of a particular dyestuff is very difficult and sometimes impossible; but the recognition of the class of dyestuff present is not so difficult. Moreover, this is what the practical dyer wants to know to enable him to match a given pattern, or to give an estimate of cost. Details of a full scheme of analysis are given by Clayton (*J. Soc. Dyers Col.*, 1937, **53**, 178) by which information about the exact nature of a dyestuff may be ascertained.

The following is an outline of a simple method for the analysis of a dyed sample:—

(1) In the case of wool or silk, a piece of the pattern is extracted with boiling alcohol or boiled with dilute acetic acid. If only traces of colour are extracted, **basic dyestuffs** are absent. If the liquid is coloured, it is tested for basic dyestuffs. The alcohol is evaporated, and the residue dissolved in a little dilute acetic acid. If acetic acid has been used as the solvent, it is expelled by boiling. The following tests are then applied: (a) a precipitate is produced by a solution of tannic acid containing sodium acetate; (b) silicotungstic acid gives a precipitate which is insoluble in dilute hydrochloric acid; and (c) tanned cotton is dyed by the cold or lukewarm solution.

In the case of cotton, the procedure is different. The sample is first soaked in a solution of sodium hydroxide saturated with salt. This decomposes the tannate of the basic dyestuff, leaving the free base on the fabric. This is squeezed, and extracted with ether. After evaporation of the ether, the residue is dissolved in dilute acetic acid, and tested as before.

(2) The pattern, after extraction with alcohol or acetic acid, is rinsed with water and boiled with dilute ammonia. Both **direct** and **acid dyestuffs** will pass into solution. The coloured extract is tested in the following manner: (a) A portion of the extract is acidified, some wool and mercerized cotton are added, and the liquid is boiled gently for half an hour. If an acid or direct dyestuff is present, the wool will be dyed and the cotton undyed. (b) Another portion of the extract is boiled until nearly all the ammonia has been expelled. Some wool and mercerized cotton are added, together with a pinch of salt; the liquid is then boiled. If an acid dyestuff is present, neither wool nor cotton will be dyed, whilst a direct dyestuff will dye the cotton but not the wool.

Direct dyestuffs may be identified also by the *bleeding test*. A piece of the material is boiled for a few minutes together with a piece of undyed cotton in water containing a little soap. A direct dyestuff will bleed on to the cotton; an acid dyestuff will not.

**Acid mordant dyestuffs** are not usually extracted by ammonia. They may be recognized by the following test: A piece of the pattern is boiled with 10 per cent. hydrochloric acid for about half an hour. This decomposes the co-ordinated compound of chromium and dyestuff, and both pass into solution.

The coloured liquid is made alkaline with ammonia, boiled, and filtered. The filtrate is acidified with acetic acid, and boiled with a little wool. The dyed wool is next boiled in a very dilute solution of potassium dichromate. If an acid mordant dyestuff is present, a change of colour or an increase in the depth of the shade will be observed. A piece of the pattern should now be burned to an ash, which is tested for chromium by the borax-bead test.

**Sulphur Dyestuffs.**—These are insoluble in acid or alkali, but can be extracted from cotton by boiling with a solution of sodium sulphide. They can be dyed back on to cotton by diluting the sodium sulphide solution and adding salt. Another test is as follows: A piece of the sample is placed in a small flask together with some tin and dilute hydrochloric acid. The mouth of the flask is plugged with lead-acetate cotton-wool, and the contents of the flask are heated gently. Sulphur dyestuffs will evolve sulphuretted hydrogen, and the cotton-wool will be stained brown or black.

**Mordant Dyestuffs.**—In the absence of other dyes, the presence of these is presumed when the material gives an ash which exceeds 1 per cent. and contains either of the metals used commonly as mordants. The oxides of those which will be present have characteristic colours, given in Table LXV.

TABLE LXV.—COLOURS OF ASHED MORDANTS.

Metal.	Oxide in Ash.	Colour of Ash.
Chromium . .	$\text{Cr}_2\text{O}_3$	Green
Iron . . .	$\text{Fe}_2\text{O}_3$	Brick-red
Copper. . .	$\text{CuO}$	Black
Aluminium . .	$\text{Al}_2\text{O}_3$	White and bulky
Tin . . .	$\text{SnO}_2$	{ Yellow when hot White when cold

**Vat Dyestuffs.**—A piece of the sample is warmed with a solution of sodium hydrosulphite and sodium hydroxide. The leuco compound of the vat dyestuff will pass into solution, and the pattern become nearly colourless. The solution of the leuco compound is spotted on filter-paper, and exposed to air. If no colour appears in half an hour, the spots are treated with dilute hydrogen peroxide solution. If, after this, still no colour appears, vat dyestuffs are absent. The reappearance of the original colour indicates the presence of a vat dyestuff.

**Azoic Colours.**—These are decomposed by reducing agents, giving a mixture of amines, which cannot be changed back into the colouring-matter by oxidation. Hence a negative result in the last test indicates the presence of an azoic colour. The nature of an azoic colour can be ascertained only by identifying the products of its reduction. Details of the methods used are given by Foster and Hanson (*J. Soc. Dyers Col.*, 1926, 42, 272) and Rowe and Leom (*ibid.*, 1924, 40, 218).

**Aniline Black.**—This may be identified as follows: When the sample is treated with a solution of bleaching powder ( $2^\circ \text{Tw.}$ ), a brown colour is produced. If a piece of the sample is dissolved in cold concentrated sulphuric acid, and the solution poured into cold water, a greenish-black precipitate or a pale green solution is produced.

It may be noted that Clayton (*loc. cit.*) recommends the use of ethylenediamine as a solvent for dyestuffs, particularly for those which contain a co-ordinated metal, such as Neolan dyestuffs. These would be decomposed also by hydrochloric acid in the method given for acid mordant dyestuffs, but would not give a different colour when treated with potassium dichromate.

**Single and Mixed Dyestuffs.**—The presence of more than one dyestuff in the extracts obtained above can be tested by the capillary test (Chapter II). The method of *fractional dyeing* may be used also. In the case of acid dyestuffs, a dye-bath is made with acid and Glauber's salt. A small piece of wool (*e.g.* 1 cm. square) is introduced into the boiling bath. When dyed, it is removed, and another piece added, the process being continued until the bath is exhausted. When only a single dyestuff is present, all the pieces will have the same colour, differing only in shade. When, however, two or more dyestuffs are present, the dyed patterns can be separated into those of the constituent colours and those having the compound colour. This test depends upon the fact that the wool will attract first that colour for which it has the greatest affinity.

## CHAPTER XXXVIII.

### THE EXAMINATION OF DYESTUFFS.

#### Identification of Class.

THE identification of the class to which a dyestuff belongs is carried out in the following manner: The solubility in water is first tested. If soluble, one of the following may be present: (i) Acid dyestuff, (ii) basic dyestuff, (iii) direct dyestuff, (iv) Neolan dyestuff, or (v) a soluble mordant dyestuff such as logwood or a bisulphite compound. If the dyestuff is insoluble, it will be either a mordant, sulphur, or vat dyestuff.

**Acid Dyestuffs.**—These dye wool from a boiling bath containing sulphuric acid and Glauber's salt, but do not dye cotton. A neutral-dyeing acid dyestuff will dye wool also from a neutral bath containing Glauber's salt, but a few of them have an affinity for cotton too. These, however, will not dye cotton from a lukewarm; slightly alkaline bath. An acid mordant dyestuff gives a precipitate when boiled with potassium dichromate; and when wool dyed with it is boiled in a bath containing a little dichromate, either a different colour or a darker shade of the same colour is produced.

**Neolan dyestuffs** dye wool from a bath containing sulphuric acid and Glauber's salt. They contain a metallic constituent, such as chromium, which can be identified in the ash.

**Basic Dyestuffs.**—Solutions of basic dyestuffs dye wool from a neutral bath or one containing a little acetic acid, but do not dye cotton unless it has been mordanted with tannic acid. A basic mordant dyestuff gives a precipitate when boiled with the chromium-fluoride reagent (10 g. of chromium fluoride and 5 g. of sodium acetate in 100 ml. of water). Aqueous solutions of basic dyestuffs give precipitates when treated with a solution of a direct dyestuff, and also with a solution of silicotungstic acid. In many cases the dye base is precipitated by a solution of sodium hydroxide containing salt. Janus dyestuffs also dye cotton from an acid boiling bath.

**Direct Dyestuffs.**—These dye both wool and cotton from a boiling bath containing salt. In the presence of acid the wool alone will be dyed, whilst in a slightly alkaline bath only the cotton is dyed. Cotton dyed with a direct dyestuff gives the bleeding test already described. Aqueous solutions of direct dyestuffs give precipitates with solutions of basic dyestuffs and with solutions of alkaloid salts, such as cinchonine sulphate.

**Soluble Mordant Dyestuffs.**—These dye neither wool nor cotton directly, but dye wool which has been mordanted with chromium sesquioxide,  $\text{Cr}_2\text{O}_3$ . They give precipitates when boiled with the chromium-fluoride reagent.

**Sulphur Dyestuffs.**—These are insoluble in water, but dissolve in water containing sodium sulphide and a little sodium carbonate. This solution dyes cotton from a boiling bath, and in most cases from a lukewarm bath. They give sulphuretted hydrogen with reducing agents, such as tin or aluminium

and hydrochloric acid. They combine with basic dyestuffs, giving insoluble compounds.

**Insoluble Mordant Dyestuffs.**—With few exceptions, mordant dyes are insoluble in water. Suspensions boiled with the chromium-fluoride reagent give coloured precipitates. They are usually polygenetic, giving precipitates having different colours with chromium, aluminium, and iron. They dye mordanted wool in a neutral or faintly acid bath.

**Vat Dyestuffs.**—These dissolve in a solution of sodium hydrosulphite containing sodium hydroxide to give yellowish solutions of the leuco compounds. These solutions, when spotted on filter-paper, give the original colour either when exposed to air or when treated with hydrogen peroxide.

### Separation of Dyes of Same Class.

Commercial dyestuffs may be mixtures of two or more dyestuffs of the same class. Mixtures can be identified by the capillary or fractional-dyeing tests already described. Separation may be effected also by chemical methods in some cases.

**Separation by means of Organic Solvents.**—It has been noted that different classes of dyestuffs have different solubilities in water and other solvents. This is true also of the different members of the same class. For example, indigoid vat colours are all soluble in boiling pyridine, while other members of the class are often insoluble. Or, again, the free dye acids which contain only carboxyl groups are soluble in ether; but if sulphonic-acid groups are present, they are insoluble in this solvent. Different members of the same class have also often differing solubility in alcohol. Thus, Cochineal Scarlet G is only slightly soluble, while Orange G dissolves freely, and a mixture of these might be separated, at any rate partly, by treating it with a limited quantity of alcohol. Details of solubilities of different dyestuffs are given in the *Colour Index of the Society of Dyers and Colourists*. In the case of acid dyestuffs, the lead salt of the dye acid is sometimes insoluble in water. If so, this can be removed by filtration, and the dye acid liberated by suspending the lead sulphonate in water and passing sulphuretted hydrogen through the mixture.

In dealing with mixtures of either acid or basic dyestuffs, a partial separation may sometimes be effected by means of ether. This is illustrated by the following examples:—

(a) **Basic Dyestuffs.**—All basic dyestuffs can be decomposed by a strong alkali, such as sodium or potassium hydroxide, and the liberated dye base is always soluble in ether. But the dyestuffs differ in the ease with which they are decomposed. They may, in fact, be classified as (i) those which are hydrolysed by water with the liberation of the dye base; (ii) those which are decomposed by weak alkalis, such as ammonia, though not by water; and (iii) those requiring a strong alkali, such as potassium hydroxide, to liberate the dye base.

Rhodamine, Victoria Blue, and Bismarck Brown are hydrolysed by water alone, and hence can be extracted from their aqueous solutions by shaking with ether in a separating-funnel. The aqueous solution would still contain the hydrochlorides of the members of the other groups. If it is made faintly alkaline with ammonia, dye bases belonging to the second group—such as magenta, indulines, oxazines, and acridines—are liberated, and can be removed by again extracting with ether. After removing these, the residual solution is treated with potassium hydroxide, which liberates all the remaining dye bases.

(b) *Acid Dyestuffs*.—J. C. Cain, J. F. Thorpe, and R. P. Linstead (*The Synthetic Dyestuffs*, 7th edn., p. 427: Griffin & Co.) classify acid dyestuffs as (i) soluble in ether in neutral solutions; (ii) soluble in ether in the presence of 1 per cent. of acetic acid; (iii) soluble in ether in the presence of hydrochloric or sulphuric acid; and (iv) insoluble in ether in the presence of acid. The first class would include unsulphonated dyestuffs which dye wool from a neutral bath, i.e. those which are hydrolysed by water. The fourth class includes all the acid dyestuffs containing sulphonic-acid groups.

**Separation by Adsorption with Kaolin.**—Suida (*Monatsh. Chem.*, 1904, 25, 1107) first studied the application of adsorption by kaolin to the separation and identification of dyestuffs. Chapman and Siebold (*Analyst*, 1912, 37, 339) investigated the problem more fully, and found that many dyestuffs were completely adsorbed from their aqueous solutions by powdered kaolin. The test is made in the following manner: A solution of the dyestuff or mixture is made of 1 g. per litre strength. Ten millilitres of this solution are stirred for 10 min. with 5 g. of powdered kaolin, previously made into a paste with water. After standing for a few minutes, the mixture is filtered through a Büchner filter or Gooch crucible by means of the pump. Dyestuffs can be divided into three classes according to their action with kaolin, viz.—

(i) Those which are completely adsorbed; (ii) those which are partly adsorbed, giving a coloured kaolin, from which the bulk of the dyestuff can be removed by washing with water; and (iii) those which are not appreciably adsorbed. Table LXVI contains a number of common dyestuffs examined by Chapman and Siebold.

TABLE LXVI.—ADSORPTION OF DYESTUFFS BY KAOLIN.

Adsorbed.	Partially Adsorbed Colour, partly extracted by washing with water.	Not Adsorbed.
Congo red, Safranine, Magenta, Neutral red, Malachite green, Brilliant green, Methylene blue, Bismarck brown, Crystal violet, Methyl violet B (extra), Auramine.	Acid green, Patent blue, Soluble blue,  All extracted by boiling water.	Acid magenta, Eosine, Erythrosine, Fluorescein, Methyl orange, Tropæoline, Orange IV, Ponceau 4R, Bordeaux R, Sudan red, Tartrazine, Naphthol yellow, Picric acid, Naphthol green, Indigo carmine, Cochineal.

In some cases a dyestuff which is itself soluble in alcohol is incapable of being dissolved out of the coloured kaolin by this solvent. This property might, in some cases, be made use of to effect the approximate separation of three dyestuffs when present together. Thus, 5 g. of kaolin having been stirred with the solution of the dyestuff, as described above, and filtered, the coloured kaolin remaining on the filter might, after one or

two washings with hot water, be treated with hot alcohol. The following are examples:—

{ Ponceau 4R . . .	Aqueous filtrate . . .	Red
{ Crystal violet . . .	Alcoholic filtrate . . .	Purple
{ Safranine . . .	Kaolin . . .	Pink
{ Naphthol yellow . . .	Aqueous filtrate . . .	Yellow
{ Magenta . . .	Alcoholic filtrate . . .	Red
{ Methylene blue . . .	Kaolin . . .	Purplish-blue
{ Fluorescein . . .	Aqueous filtrate . . .	Dirty pink and fluorescent
{ Brilliant green . . .	Alcoholic filtrate . . .	Green
{ Congo red . . .	Kaolin . . .	Pink

### Green's Method of Analysis.

The practical dyer does not, as a rule, want to know more of a dyestuff than the class to which it belongs. But if he does, further information may be obtained by Green's method of analysis, which is based upon the reduction of the substance by means of zinc dust and acetic acid. When treated with reducing agents, dyestuffs are either decolorized partly or completely, or not at all. If they are decolorized, the colour is sometimes restored on exposure to air, sometimes only on treatment with a strong oxidizing agent, and sometimes not at all. This depends upon the chemical constitution of the dyestuff, and thus separation into certain chemical groups is made possible. These groups are similar to those given in the last chapter for the identification of dyestuffs on the fibre, but zinc dust is used as the reducing agent, and acidified potassium permanganate as the oxidizing agent. The reduction test is made as follows:—

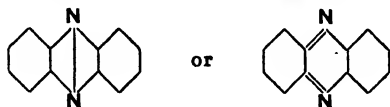
A little hot solution of the dyestuff is placed in a test-tube, and sufficient fresh zinc dust to cover the top of a penknife is added. After mixing, a few drops of 5 per cent. acetic acid are added till decolorization occurs. After a minute or two, the clear solution is poured on to a filter-paper, and exposed to air. If the colour does not return in a minute or two, the paper is touched with a glass rod dipped in acidified potassium permanganate solution, made by

TABLE LXVII.—REDUCTION OF DYES WITH ZINC.

Decolorized by Zinc Dust.			Unaltered by Zinc Dust or reduced only slowly and partially.	Not decolorized by Zinc Dust, but changed in shade completely.
Colour restored on Exposure to Air.	Colour restored only by Oxidizing Agents.	Colour restored by neither Air nor Oxidizing Agents.		
Azines, Oxazines, Thiazines, Indigoids, Pyrones (violet and blue), Acridines.	Triphenyl- methane dyes, Pyrone (red).	Nitro, nitroso, and azo dyes.	Quinolines, Thiazoles.	Anthracene dyes.

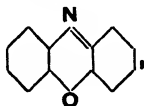
dissolving 1 g. of permanganate and 2 g. of sulphuric acid in a litre of water. Warming the paper assists the re-oxidation. The indications given by this test are classified by Green as in Table LXVII.

The *azine* dyestuffs are derivatives of phenazine—



The eurhodines, aposafranines, safranines, indulines, and nigrosines belong to this class.

The *oxazines* contain the grouping—



and include Meldola's Blue and Nile Blue A.

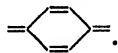
The *thiazines* are represented by Methylene Blue—



The *indigoids* are all similar to indigo, and contain the chromophore  $\text{CO}:\text{C}:\text{C}:\text{CO}$ .

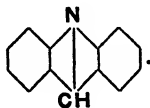
The *triphenylmethane* dyestuffs are derived from triphenylmethane,  $\text{CH}(\text{C}_6\text{H}_5)_3$ . Magenta, Methyl Violet, Victoria Blue, and Malachite Green are common examples. They all contain the para-quinone grouping.

The *pyrone* dyestuffs contain the para-quinone grouping—

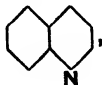


They include the pyronines, phthaleins, galleine, and cœruleine.

The *acridine* colours are derived from acridine—

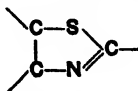


Quinoline,



gives rise to such dyestuffs as Quinoline Blue.

The *thiazole* dyestuffs contain the grouping—



Primuline and thioflavine are examples.



The *anthracene* dyestuffs include colours derived from anthracene, such as the alizarines, and which are not vat dyestuffs derived from anthraquinone.

If the dyeing class is known, and also the group to which the dyestuff belongs, the practical dyer will generally be able to choose suitable colours to match his pattern. If the fabric is composed of only one fibre, the solution of the problem is now not very difficult. But in a large number of cases two or even three fibres may be present. This complicates the problem considerably, since different fibres have varying affinities, even for a dyestuff which will dye both.

### The Analysis of Commercial Dyestuffs.

Commercial dyestuffs may contain various impurities, either added as diluents or not removed completely during manufacture. These include sulphates, chlorides, carbonates, and organic matter other than dyestuff. Sometimes insoluble matter may be present also. The following is an outline of the methods used for a general chemical analysis of dyestuffs which are soluble in water.

**Determination of Insoluble Matter.**—About 1 g. of the sample is weighed, boiled with distilled water, and filtered through an asbestos mat on a weighed Gooch crucible. The residue on the filter is washed with small quantities of hot water until no more colour is extracted. The crucible is then dried at 100° C., cooled in a desiccator, and weighed. It is then heated over a Bunsen flame until any organic matter is destroyed, after which it is cooled, and weighed again. The residue will give inorganic impurities, whilst the difference between the first and second weighings gives the organic matter other than dyestuff.

**Examination of the Filtrate.**—The filtrate is cooled, and diluted to a definite volume with water.

**Sulphates** are determined in an aliquot part of the filtrate by adding a little hydrochloric acid and excess of barium chloride solution. After standing for several hours, the precipitated barium sulphate is filtered off on an asbestos mat in a weighed Gooch crucible, dried, ignited gently, and weighed. Allen's method may be used also: The precipitate obtained with barium chloride is filtered off and washed. It is then boiled with ammonium carbonate, when any barium sulphonate present will be dissolved, the barium sulphate remaining unchanged. This is filtered off, washed with dilute hydrochloric acid, then with water, dried, ignited, and weighed.

**Chlorides** are determined in another portion of the solution by titration with Votek's mercuric nitrate solution. This is a standard solution of mercury in a slight excess of nitric acid, which forms with chlorides a compound having the formula  $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{MCl}$ . The solution to be titrated is made slightly acid with nitric acid, and 0.06 g. of sodium nitroprusside is added as an indicator. The solution containing the chloride is then run in from a burette until a faint turbidity is produced. The mercuric nitrate solution is standardized with pure sodium chloride.

**Carbonates** are identified by treating a little of the original dyestuff with hydrochloric acid in a flask or test-tube provided with a delivery tube which dips beneath the surface of some lime-water.

When dealing with a basic dyestuff, it is better to use alcohol as the solvent instead of water. In this case, salts will be left on the asbestos mat, from which they are removed by treatment with water.

**Determination of Heavy Metals.**—A weighed quantity of the dyestuff is heated with concentrated sulphuric acid in a Kjeldahl flask until it is dissolved. About 5 g. of potassium sulphate is then added, and the heating continued until a colourless solution is obtained. From time to time the liquid is allowed to cool, and a drop of perchloric acid added to assist oxidation. When oxidation is complete, the contents of the flask are cooled, and diluted carefully with cold water. Lead sulphate or barium sulphate, if present, will be precipitated, and, after standing for some time, can be filtered off on a Gooch crucible, and weighed. The filtrate is made up to a definite volume, and tested for other heavy metals, such as copper or iron, in the usual manner.

**Determination of the Dyestuff.**—The percentage of dyestuff can often be inferred. If the percentages of moisture and ash are known, the sum of these deducted from 100 will give the approximate percentage of dyestuff, but allowance must be made for the sulphonate groups in a sulphonated dyestuff. There are, however, special methods of analysis, which include the following:

(1) Acid dyestuffs can be determined by titration with a standard solution of a basic dyestuff having a different colour. Similarly, basic dyestuffs can be determined by titration with an acid dyestuff.

(2) All dyestuffs which are decomposed by reducing agents can be determined by titration with a standard solution of titanous chloride.

(3) Direct dyestuffs give insoluble precipitates with salts of alkaloids such as cinchonine. These can be separated and weighed.

(4) Similarly, basic dyestuffs give insoluble compounds of definite composition with silicotungstic acid.

(5) In some cases special methods are used. Thus Indigo Carmine can be determined by titration with a standard solution of potassium permanganate.

**Titration of Acid and Basic Dyestuffs.**—*Basic Dyestuffs.*—Auramine can be titrated with a solution of indigo carmine. One gram of the basic dyestuff is dissolved in a little dilute acetic acid, and the solution made up to 500 ml. A second solution of 1 g. of indigo carmine is made of the same strength. This is run into a measured volume of the auramine solution from a burette. Spots on filter-paper made at intervals show a yellow ring, which disappears gradually as the indigo carmine is added, the end-point being marked by the first appearance of a blue ring.

In some cases in which the end-point is not very definite, a mixed solution of the acid dyestuff and tannic acid is employed. The precipitate formed in the presence of tannic acid is more granular, and makes the end-point more definite. For example, Brilliant Green and Malachite Green are titrated with a solution of Orange II containing 1 g. of Orange II, 2 g. of tannic acid, and 2.5 g. of sodium acetate per litre. 25 ml. of the green solution are titrated until no further precipitate is formed, this point being indicated by the appearance of an orange ring on the filter-paper. Magenta is titrated in the same way. The methods for other common basic colours are—

Dye.	Precipitant.
Methyl violet . . . . .	Naphthol yellow
Methylene blue . . . . .	Crystal scarlet and tannic acid
Rhodamine B and 6G . . . . .	Metanil yellow and tannic acid
Safranine . . . . .	Tartrazine

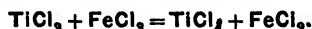
*Acid dyestuffs* are titrated in the same way with a basic dyestuff.

**Titration of Direct Dyestuffs.**—These may be titrated with suitable basic colours, but in many cases excess of the basic dye is added, and the unused portion determined by back-titration with an acid dyestuff. For example,

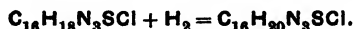
Benzopurpurine and Chrysophenine are treated with excess of a standard solution of Auramine, and the residual basic dye titrated with Orange II.

**Titration with Titanous Chloride.**—This method is due to E. Knecht, and full details may be obtained from *New Reduction Methods in Volumetric Analysis*, by E. Knecht and E. Hibbert.

Titanium forms four oxides: titanium monoxide,  $\text{TiO}$ ; titanium sesquioxide or titanous oxide,  $\text{Ti}_2\text{O}_3$ ; titanium dioxide,  $\text{TiO}_2$ ; and titanium peroxide,  $\text{TiO}_3$ . Titanous oxide gives rise to titanous salts, such as titanous chloride,  $\text{TiCl}_3$ . This salt is a very powerful reducing agent, being itself at the same time oxidized to the tetrachloride,  $\text{TiCl}_4$ ; thus, with ferric salts:



Not only are inorganic compounds reduced by titanous chloride, but organic bodies also. In the case of the dyestuffs this reduction is accompanied generally by the formation of a leuco compound; thus, with methylene blue:



Every dyestuff which forms a leuco compound or is decolorized by reduction can be estimated by titration with a standard solution of titanous chloride.

There are certain difficulties connected with the process. The titanous chloride solution has to be kept in contact with hydrogen to keep it from being oxidized, and it must be frequently standardized. The titration also must be carried out in the presence of an inert gas such as carbon dioxide. The following brief account is taken from Knecht's book:—

**Preparation of Solutions required.**—*Titanous Chloride.*

—Fifty millilitres of commercial (20 per cent.) titanous chloride solution are boiled for a minute with 100 ml. of concentrated hydrochloric acid in a small flask. The solution is cooled, and made up to about 2.25 litres with air-free water. This is placed in the bottle *a* (Fig. 192), and the solution should fill the bottle up to the neck. This bottle or store tank is connected with a burette *b*, and also with a hydrogen-generating apparatus *d*. At *c*<sub>1</sub> and *c*<sub>2</sub> are lead valves inside rubber-tubing connections. The inner tube of *d* contains zinc, and the outer cylinder a mixture of equal volumes of water and hydrochloric acid. At the bottom of the tube containing the zinc is a small aperture for the entrance of the acid. When the valve *c*<sub>2</sub> is opened, the acid attacks the zinc and liberates hydrogen, thus keeping the system full and preventing oxidation of the titanous chloride.

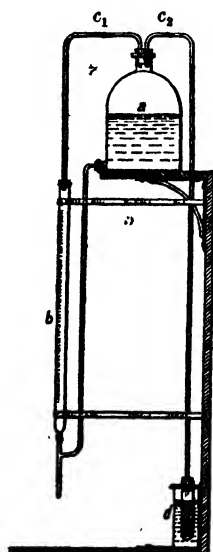


Fig. 192.—Apparatus for Titrations with Titanium Chloride.

*Ferric Alum Solution.*—About 14 g. of ferric alum are

dissolved in water acidified with sulphuric acid, and made up to 1 litre.

**Standardization of Titanous Chloride Solution.**—In order to standardize the titanous chloride solution, 25 ml. of the iron alum solution is placed in a flask, together with some potassium thiocyanate as an indicator. The titanous chloride solution is then run in till the red colour due to ferric thiocyanate just disappears. This indicates that all the ferric iron has been reduced. Since the quantity of ferric oxide taken in the 25 ml. of the iron alum solution is known, the strength of the titanous chloride solution can be calculated in terms of iron which it reduces.

**Estimation of Dyestuffs with  $\text{TiCl}_3$ .**—Many dyestuffs can be estimated directly, e.g. methylene blue. But in other cases excess of titanous chloride solution is added, and the unused portion determined by back-titration with the standard iron solution. But the titration must be conducted in an atmosphere of carbon dioxide at the boiling-point. A suitable flask for this titration is illustrated in Fig. 193. The tube within the cylinder contains broken marble, and the cylinder hydrochloric acid. The following are examples of the methods employed:—

**Methylene Blue.**—Dissolve 1 g. of the substance in 250 ml. of water. Fifty millilitres of this solution are placed in the titration flask, and a little hydrochloric acid added. Carbon dioxide is then passed through the apparatus, and the contents of the flask heated over a Bunsen burner. The titanous

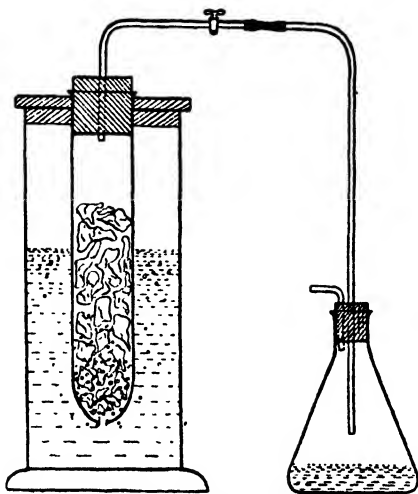
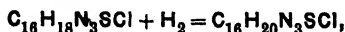


Fig. 193.—Titration Flask.

chloride solution is run in till the blue colour just disappears. From the equation:



it is evident that 319.5 parts of methylene blue are equivalent to 112 of iron.

**Magenta.**—In some cases the presence of Rochelle salt or sodium tartrate is necessary for the production of the leuco compound. In estimating magenta, 50 ml. of a solution of 1 g. of the dyestuff in 500 ml. of water are placed in the flask with 25 ml. of a 20 per cent. solution of Rochelle salt. The mixture is then boiled, and titrated in a current of carbon dioxide.

**Benzopurpurine on dyed cotton by back-titration.**—A weighed quantity of the sample is placed in the titration flask, and boiled with dilute hydrochloric acid. Carbon dioxide is then passed in, and a measured excess of the titanous chloride solution is added. The flask is then heated till the colour of the dyestuff has disappeared. It is then cooled, and the excess of titanous chloride solution titrated with standard iron alum solution, using potassium thiocyanate as indicator. One part of Benzopurpurine 4B is equivalent to 0.618 part of iron.

**Quantity of dyestuff taken up by a sample of wool.**—In this case the dyestuff cannot be titrated on the fibre, but that remaining in the dye-bath is mixed, and the quantity absorbed obtained by difference.

**Determination of Direct Dyestuffs.**—All direct dyestuffs form precipitates with alkaloids which have a definite composition. Thus Chrysophenine gives  $C_{30}H_{20}O_2N_4(SO_3H)_2B$ , where B represents a molecule of the alkaloid base. The reagent used is cinchonine sulphate. A weighed quantity of the dyestuff is dissolved in water, and excess of a cold saturated solution of cinchonine sulphate is added. The mixture is heated on a water-bath until the precipitate coagulates. It is then filtered through an asbestos mat in a weighed Gooch crucible, washed with a cold saturated aqueous solution of cinchonine sulphate, dried at  $120^\circ$  to  $130^\circ$  C., and weighed. For full details consult Trotman and Frearson (*J. Soc. Dyers Col.*, 1931, 47, 345) and Trotman and Horner (*ibid.*, 1933, 49, 256).

**Determination of Basic Dyestuffs.**—All basic dyestuffs give precipitates with silicotungstic acid which are insoluble in water or dilute boiling hydrochloric acid. About 0.2 g. of the dyestuff is dissolved in dilute hydrochloric acid, excess of an aqueous solution of silicotungstic acid is added, and the mixture boiled to coagulate the precipitate. The latter is then filtered off in a weighed Gooch crucible, washed with water, dried at  $105^\circ$  to  $110^\circ$  C., and weighed. The crucible is next ignited, and weighed again. The residue consists of  $SiO_2 \cdot 12WO_3$ . The difference between the two weights gives the dye base present in the dyestuff taken.

**Special Methods for Certain Dyestuffs.**—The determination of indigo is an example: a weighed quantity of the substance is warmed with concentrated sulphuric acid, with which it forms indigotin-disulphonic acid. This is dissolved in water, and the solution diluted to a known volume. An aliquot part of this solution is diluted to about 750 ml. in a porcelain dish, and titrated with a decinormal solution of potassium permanganate, the end-point being indicated by the production of a golden-yellow colour, due to isatin-disulphonic acid. Each millilitre of 0.1N. potassium permanganate solution oxidizes 0.00755 g. of indigo.

### Dyeing Tests.

**Comparison of the Dyeing Values of Two Dyestuffs.**—Solutions of each are made of exactly the same strength, e.g. 2.5 g. per litre. Assuming that the dyestuffs are acid dyes, the test could be made as follows: Two 5- or 10-g. skeins of wool are taken. Two dye-baths are then made up with exactly the same quantities of dyestuff (say 4 per cent.), sulphuric acid, Glauber's salt, and water. The skeins are then entered at  $140^\circ$  F. ( $60^\circ$  C.), and dyed in the usual manner. They are then removed, the excess of dye liquor is squeezed back into the bath, and the skeins are rinsed and dried. The colours are then compared. If both are identical, the dyeing values are the same. If one is lighter in colour than the other, it is put back into the bath in which it was dyed, a small but known volume of the dye solution is added, and dyeing is continued. More of the dye solution is added, if necessary, till the shade matches that of the other sample. The weights of the dyestuffs used to give identical shades are known from the volumes of the solutions added to the baths. These quantities vary inversely with the dyeing values. Thus, if twice as much were used in one bath as the other, the dyestuff would have half the dyeing value.

In the case of mordant dyestuffs, mordanted wool must be used. The method has been described for logwood.

**Comparison of the Exhausting Powers of Two Dyestuffs.**—Two flasks with 250-cc. necks are taken, each having a mark indicating a convenient volume, say 200 ml. Assuming that the colours to be compared are acid dyestuffs,

the following procedure could be adopted: Exactly the same volume of a standard solution of each dyestuff is placed in each flask, followed by the same quantities of sulphuric acid and sodium sulphate. A skein of wool weighing 5 g. is then wetted down and introduced into each flask, after which the volume is made up to the mark with distilled water. The flasks are then placed in a bath of boiling water, and dyed for half an hour at 100° C. The skeins are then removed, and the excess of dye liquor is squeezed back into the flask. The skeins are then rinsed, and dried. Sufficient distilled water is added to each flask to bring its volume up to the mark, and then two more skeins are introduced, dyed, and treated as before. This is continued with fresh skeins till no more dyestuff is taken up.

**Determination of Equalizing or Levelling Power.**—As a general rule, quick-dyeing colours are more unlevel than those which are absorbed less rapidly by the fibre. The following method for testing equalizing power may be used: A piece of the fabric is bound tightly in one place, and then dyed under the usual conditions. The bound part is then untied, and the piece put back into the bath. If the dyestuff has good equalizing properties, the bound portion will dye up to the same shade as the rest of the sample. With a bad equalizer, it will remain lighter in shade.

**Comparison of the Tinctorial Values of Two Dyestuffs.**—Standard solutions of the same strength are made up either with water or with alcohol. A known volume of the standard dyestuff is placed in a Nessler cylinder, and diluted with water or spirit to 50 ml. The volume of the second dyestuff necessary to match the colour is then found by trial and error, using a second Nessler cylinder, and diluting each time to 50 ml.

## CHAPTER XXXIX.

### DAMAGE AND DEFECTS.

BOTH undyed and dyed goods are liable to show damage or defects. In the case of undyed materials, these consist generally of discolorations, general loss of colour, or mechanical defects such as small holes or tenderness. In dyed goods, the same faults may occur, and in addition unevenness in the distribution of the dyestuff, which may appear as barriness or localized differences in colour. These defects may be classified as due to the following:—

- (1) Inherent defects in the original fibres or material.
- (2) Faulty processing in spinning, knitting, or weaving.
- (3) Faults in scouring or bleaching.
- (4) Faulty dyeing.
- (5) Accidental damage, such as scorching or from mechanical agencies.

It is impossible to give a complete list of these defects, but some of the most important may be noted.

**Defects due to the Original Fibre.**—In the case of artificial fibres these have been described already. With cotton, the presence of either dead or unripe fibres will generally cause uneven dyeing or mercerization, whilst mildew is an occasional cause of trouble in both cotton and woollen goods. Wool which has been exposed to sunlight has an altered affinity for dyestuffs, whilst the presence of kempy fibres, or skin wool, acts in a similar manner.

**Defects due to Faults in Preparing or Spinning.**—In the case of wool, damage may be caused during carbonization, which will subsequently be responsible for uneven dyeing. The use of hard water in scouring may precipitate insoluble soaps in the fibre, whilst a rancid oil in spinning will give rise to hydroxy fatty acids. Traces of metals may be derived from machines, and these cannot be removed by subsequent scouring.

**Faults occasioned by Weaving and Knitting.**—Differences in tension during either weaving or knitting may cause uneven dyeing. Dyed woven goods sometimes show light or dark streaks or patches termed *lists*; these are connected with tightness of weaving. Knitted goods may have similar defects. The use of an unsuitable lubricating mixture in knitting may cause subsequent trouble, owing to the presence of unsaponifiable oil or the development of rancidity.

**Faulty Scouring and Bleaching by the Dyer.**—Flocons may be produced in silk during the boiling-off process. If present, they cause unevenly dyed spots or patches. In these and other goods incomplete removal of soap after scouring, and in the case of wool the use of a high-titer soap or of one containing rosin, will cause trouble subsequently. Hard water, which precipitates insoluble calcium or magnesium soaps in the goods, inhibits penetration of dye liquors. The following is an example of a woollen fabric which

died unevenly: it contained 0.73 per cent. of oil, 1.88 per cent. of soap, and 0.25 per cent. of calcium soap. The use of calgon in decomposing calcium and magnesium soaps has been described in Chapter VI.

According to Midgley (*J. Soc. Dyers Col.*, 1922, **38**, 181), marks, lines, or streaks running irregularly in the longitudinal direction of pieces are sometimes caused by overcrowding in the scouring machine or by the use of too little liquor. Either of these might make it impossible for the goods to change their positions, keeping them more or less in the same folds throughout. These defects cause streakiness when the goods are dyed. He suggests also that uneven shrinkage or excessive or insufficient tension during crabbing may also cause similar results, and, with more certainty, that the artificial conditioning of yarns on bobbins has such effects. When the yarn is treated with conditioning solutions, the outer layers absorb it all, and the layers beneath the surface are held tightly by these, so preventing the solution from penetrating. Also the pressure of one layer on another prevents the fibres from altering their position, and tends to set or fix them in the positions they occupy. This is accentuated by such bodies as soluble oils, which have marked hygroscopic properties.

Damage may be caused during bleaching. The effect of metallic catalysts has been noted already. Loss of tensile strength or small holes are often caused by the presence of iron or copper. Holes may have also a mechanical origin. In this case the ends of the fibres, if examined with a microscope, will generally appear undamaged, and at right angles to the axis of the fibre. If the holes are due to the action of chemicals, the fibre ends will have a rounded or blunt appearance. Sometimes in the case of wool the cortical cells may be seen protruding from the end of the fibre. The detection of mechanical damage in cotton by the Congo-red test has been described above.

**Defects due to Faults committed in Dyeing.**—Uneven shades may be due to any of the following causes:—

(1) Entering goods into the bath at too high a temperature. This refers to all fibres. Goods should never be entered at a temperature at which the fibre develops its maximum affinity for the dyestuff. This results in rapid surface-dyeing, before the liquor has penetrated the material. Rapid dyeing is likely to give uneven shades and colours that rub off easily.

(2) Heating the bath up too rapidly after entering the goods. Thus, in dyeing wool with acid dyestuffs, it should take half an hour to raise the temperature from 140° F. (60° C.) to the boiling-point.

(3) Not continuing the boiling for a sufficient length of time to permit equalization.

(4) The sudden addition to the bath of acids, of assistants, or of dyestuffs without lifting the goods, or the addition of solid chemicals instead of their solutions.

(5) In the case of the after-chromed dyestuffs, not allowing to cool off before adding potassium dichromate.

(6) Insufficient circulation of the dye liquor or the goods, particularly in the case of heavy pieces, or such things as cops or cheeses difficult to penetrate.

(7) Allowing dyed goods to lie about without squeezing out the dye liquor and rinsing, or in some cases insufficient soaping to remove any loosely-attached surface dyestuff.

(8) Inequalities of tension in dyeing piece-goods in the open width, or uneven nips in machines.



*Localized stains, patches, or spots produced in dyeing* may be due to the following causes:—

(a) The presence of particles of undissolved dyestuff, which attach themselves rapidly to the surface of the goods.

(b) The use of hard water. For example, in the case of the basic dyestuffs, this might cause precipitation of the dye base on the fabric. When soap is added to a dye-bath as an assistant, hard water would give rise to calcium and magnesium soaps. The effects of these would be the same as those due to incomplete preliminary scouring.

(c) Metallic stains, due to iron, copper, or lead derived from dyeing vessels or pipes.

(d) Oil stains.

(e) Accidental splashes of dye liquors or solutions of chemicals while handling the goods, or after they are dyed.

(f) Uneven mordanting, or, in some cases, allowing mordanted goods to lie about exposed to light or air between mordanting and dyeing.

(g) Mildew stains, caused by letting dyed goods lie in a damp, warm atmosphere.

**Removal of Stains.**—*Iron Stains.*—These may be removed by treatment with oxalic acid or potassium hydrogen oxalate, followed by washing with water. Hydrofluoric acid acts in a similar manner.

*Copper Stains.*—These can be removed by a dilute solution of potassium cyanide.

*Oil Stains.*—The stained portion of the fabric is padded with a mixture of Turkey-red oil or other sulphonated soap and an organic solvent such as trichlorethylene, and allowed to stand for a short time. It is then washed with warm water.

*Mould Stains.*—Stains caused by moulds or bacteria are very difficult to deal with, but sometimes they respond to the treatment given for oil stains.

**Tenderness in Dyed Goods.**—This is confined chiefly to silk, rayon, and cotton. In all it may be caused by unremoved mineral acid. The tendering of weighted silk has been fully discussed. Cotton dyed with aniline black is sometimes tendered by the action of unremoved traces of the oxidizing agent or oxygen-carrier used. Sulphur dyestuffs may also give rise to tendering, especially if an oxygen-carrier is present, by the oxidation of loosely-combined sulphur. All dyed goods are tendered by the growth of moulds or certain kinds of bacteria.

When goods are dyed unevenly, the following procedure may be adopted: They are treated carefully with a suitable stripping-agent until most of the dyestuff has been removed. They are then washed thoroughly, neutralized if necessary, and redyed very carefully. If they now dye evenly, the fault was due to the dyer, but if they still dye unevenly, the goods are to blame.

There are certain unclassifiable defects, such as scorch marks, caused by accidental contact with hot pipes, or splashes of chemicals. White cotton goods sometimes develop a pink colour if kept in the neighbourhood of aniline black.

## CHAPTER XL.

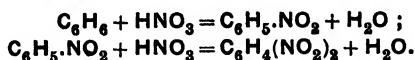
### THE PREPARATION OF DYESTUFFS.

SEVERAL examples of the methods used in the preparation of dyestuffs have been given already, and the syntheses of alizarine and indigo have been described. In the following pages a few other typical dyestuffs, which are comparatively easy to prepare, will be dealt with.

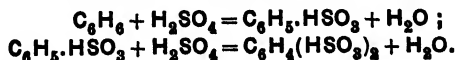
The separation of coal-tar hydrocarbons has been discussed in Chapter I, and their conversion into intermediates explained. In the preparation of these bodies, and in the building up of dyestuffs from them by the introduction of chromophore and auxochrome groups, certain general reactions are commonly employed. Some of these have been referred to, but it will be convenient to restate them, and to add one or two others of importance.

The chief reactions concerned in the manufacture of intermediates and dyestuffs are the following:—

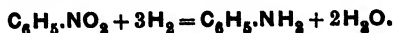
(1) **Nitration.**—The object of this process is to introduce one or more nitro ( $-\text{NO}_2$ ) groups into an organic compound in place of an equal number of hydrogen atoms. The compound to be nitrated is treated either with nitric acid or with a mixture of nitric acid and sulphuric acid, the latter acting chiefly as a dehydrating agent. The number of nitro groups introduced depends upon the conditions of the reaction. Thus, benzene gives firstly nitrobenzene,  $\text{C}_6\text{H}_5\cdot\text{NO}_2$ , and, if this be further nitrated at a high temperature, dinitrobenzene,  $\text{C}_6\text{H}_4(\text{NO}_2)_2$ :



(2) **Sulphonation.**—This consists in treating an organic compound with sulphuric acid or sulphuric acid containing free sulphur trioxide (fuming sulphuric acid) in order to introduce sulphonic-acid groups ( $-\text{SO}_3\text{H}$ ). As with nitration, the number of sulphonic-acid groups introduced depends upon the reaction conditions. Thus, with benzene, either a monosulphonic acid,  $\text{C}_6\text{H}_5\cdot\text{HSO}_3$ , or a disulphonic acid,  $\text{C}_6\text{H}_4(\text{HSO}_3)_2$ , may be obtained, according to the temperature of the reaction and the proportion of acid used:

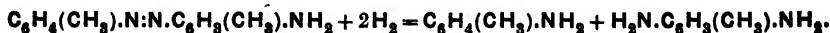


(3) **Introduction of Amino ( $-\text{NH}_2$ ) Groups.**—This is generally effected by reduction of a nitro compound with tin and hydrochloric acid, or iron and acetic or hydrochloric acid. Thus nitrobenzene gives aniline:



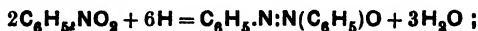
Amino groups may be introduced also by reducing an azo compound, but in this case the compound is broken up into two or more amines. Thus

aminoazotoluene, when reduced, gives a mixture of *o*-toluidine and *p*-toluylendiamine:

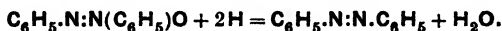


(4) **Introduction of Azo ( $-\text{N}:\text{N}-$ ) Groups.**—This is brought about by diazotization, which has been described fully. Occasionally azo groups may be introduced by other methods. Thus, when a nitro compound is reduced by means of certain alkaline reducing agents, such as sodium amalgam in the

presence of water, azoxy compounds, containing the group  $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{N}-\text{N} \end{array}$ , are first formed, and these, when reduced further, are changed into azo compounds. Thus, with nitrobenzene:

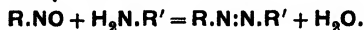


Azoxybenzene



Azobenzene

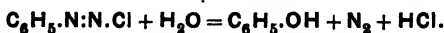
Sometimes, also, an azo group may be produced by the condensation of an amine with a nitroso compound; thus:



(5) **Introduction of Hydroxyl ( $-\text{OH}$ ) Groups.**—When the sodium salt of a sulphonic acid is fused with sodium hydroxide, the sulphonic-acid group is replaced by hydroxyl, and sodium sulphite is also formed. Thus, with  $\alpha$ -naphthalene-sulphonic acid,  $\alpha$ -naphthol is obtained:

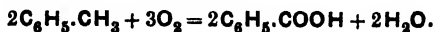


Hydroxyl groups may be introduced, also, by boiling a diazonium salt with water. Thus, diazobenzene chloride gives phenol:

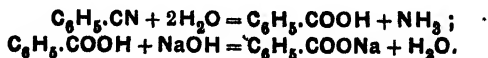


(6) **Carboxyl ( $-\text{COOH}$ ) Groups.**—These are introduced, commonly, in one of the following ways:—

(a) By the oxidation of a side chain attached to an aromatic residue. For example, when toluene is oxidized with a mixture of manganese dioxide and sulphuric acid, benzoic acid is formed:



(b) By subjecting a nitrile (*i.e.* a compound containing the  $-\text{CN}$  group) to hydrolysis by heating with a solution of a dilute acid or alkali. In the latter case the alkali salt of the carboxylic acid is formed, and the nitrogen is given off as ammonia. Thus, with benzonitrile:

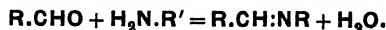


If the hydrolysis is brought about by means of a dilute mineral acid, the ammonium salt of the organic acid is obtained:



## THE PREPARATION OF DYESTUFFS.

(7) **Condensation with Elimination of Water.**—This is a reaction which is often made use of. It is the opposite to hydrolysis. Thus, when an aldehyde is heated with a body containing an amino group, in the presence of sulphuric acid (or other condensing agent, such as zinc chloride), one molecule of water is formed, and the residues combine or *condense* (see Malachite Green, below).



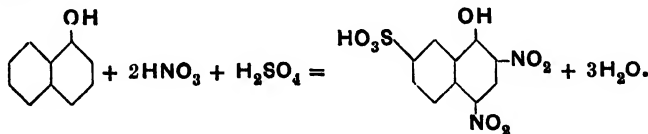
(8) **Coupling.**—This is by far the most important reaction in the manufacture of dyestuffs, as will be seen from the following examples. The reaction has been explained fully in previous chapters.

Some detailed examples of the methods used in the preparation of dyestuffs will now be given. These will illustrate also the chief differences in the members of the various dyeing classes. In the descriptions given the following works have been made use of, and these may be studied for further examples:

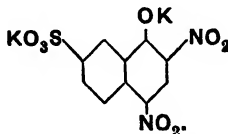
- (i) *The Colour Index of the Society of Dyers and Colourists.*
- (ii) *Synthetic Dyestuffs*, by Cain, Thorpe, and Linstead, 7th ed. (Griffin & Co.).
- (iii) *Organic Chemistry*, by Perkin and Kipping.

### Acid Dyestuffs.

**Naphthol Yellow S.**—One hundred grams of  $\alpha$ -naphthol are added, in small pieces, all at once, to 222 ml. of concentrated sulphuric acid in a round flask heated to 100° C. The temperature of the mixture is raised to 120° C., and maintained at this point for three or four hours. The mixture is then poured into 600 ml. of water, and stirred mechanically. As soon as the temperature has fallen to about 30° C., the solution is poured into a mixture of 90 g. of nitric acid with 33 ml. of water, the temperature being kept below 35° C. A further 84 g. of nitric acid is added, during which addition the temperature may rise to 40° C. The mixture is filtered on a woollen cloth, and washed with salt solution till free from acid. The drained paste is stirred with hot water at 80° C., sodium carbonate added till it is neutral, and the dyestuff precipitated by adding about 75 g. of potassium chloride. It is filtered and dried on a porous plate:

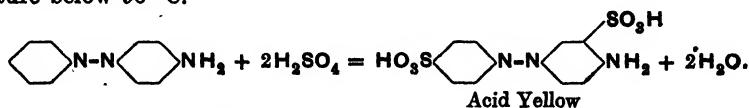


When precipitated with potassium chloride, the sulphonic-acid group is neutralized, giving

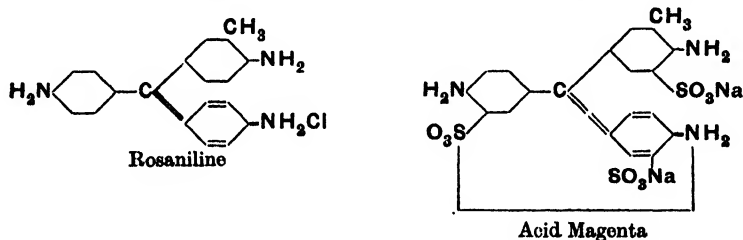


**Acid Yellow (sulphonation of aminoazobenzene).**—One part of dry aminoazobenzene hydrochloride is stirred with 4 to 4.5 parts of fuming sulphuric acid (containing 25 per cent. of sulphur trioxide) at 40° C. till the product dissolves completely in dilute ammonia. The mixture is then poured into 100 parts of dilute brine of specific gravity 1.06. The sulphonic acid is filtered

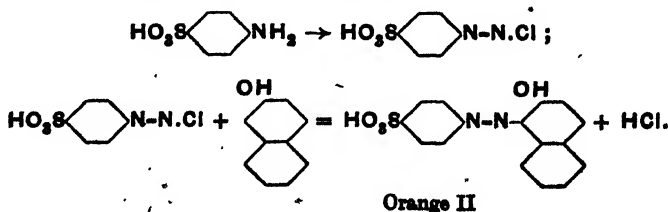
off, washed with brine, and converted into the sodium salt by dissolving it in sodium carbonate solution and evaporating the solution to dryness at a temperature below 90° C.



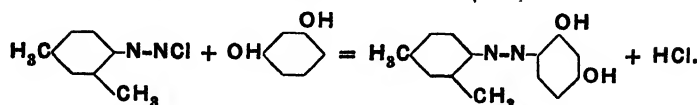
**Acid Magenta (sulphonation of magenta).**—Ten grams of rosaniline dried at 110° C. are added gradually with good agitation to 40 g. of fuming sulphuric acid (20 per cent.  $\text{SO}_3$ ), the temperature of the mixture being maintained between 120° and 170° C. When sulphonation is complete, the viscous product dissolves readily in water, and a clear yellowish solution with no precipitate is obtained on the addition of excess of alkali. The product is then mixed with water, and the solution neutralized with milk of lime. The solution of the readily soluble calcium salts of the sulphonic acids is filtered from the calcium sulphate, converted into the sodium salts with soda, and evaporated to dryness. But the product is hygroscopic, and it is preferable to convert into the acid sodium salt by adding hydrochloric acid to the solution of the sodium salt until it acquires a strong red colour, and then evaporating to dryness:



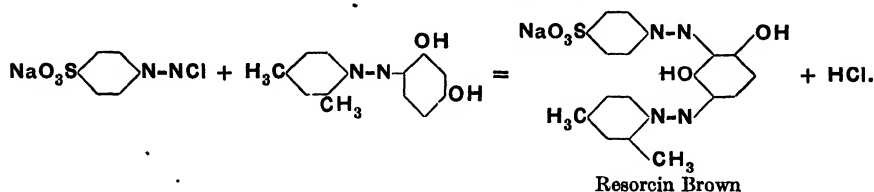
**Orange II (monazo acid dyestuff).**—17.3 g. of sulphanilic acid are dissolved in water by the careful addition of sodium hydroxide solution. The solution is cooled, and 30 ml. of concentrated hydrochloric acid added, followed by 7.2 g. of sodium nitrite dissolved in a little water. The sodium nitrite is added slowly with stirring, and a slight excess of nitrous acid must be present at the end of the operation. This is tested for by means of starch-iodide paper. The diazo compound separates out in fine white needles. 14.4 g. of  $\beta$ -naphthol are dissolved by heating with 4.5 g. of sodium hydroxide and 15 ml. of water. The solution is poured into 160 ml. of water, and the diluted solution cooled to 15° C. The diazotized sulphanilic acid is run into this solution with constant stirring. After adding the whole of the diazo solution, the mixture should show a faintly alkaline reaction to Brilliant Yellow paper. The mixture is stirred for an hour, and a little salt is added to aid the precipitation of the dyestuff. The precipitate is filtered off, and dried at 80° C.:



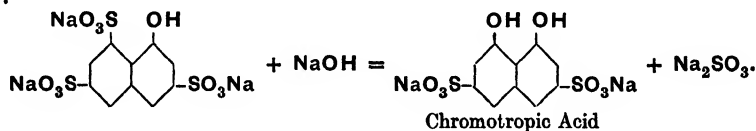
**Resorcin Brown** (*disazo acid dyestuff*).—12.1 g. of *m*-xylidine are diazotized, and coupled with 11 g. of resorcinol:



17.3 g. of sulphanilic acid are then diazotized, and coupled with the solution of the compound produced by the first reaction, dissolved in dilute sodium hydroxide solution. The dyestuff is then salted out:

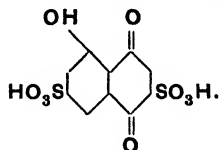


**Chromotropic Acid** (*acid sodium salt of 1 : 8-dihydroxy-naphthalene-3 : 6-disulphonic acid*).— $\alpha$ -Naphthol-3 : 6 : 8-trisulphonic acid is fused with caustic soda:

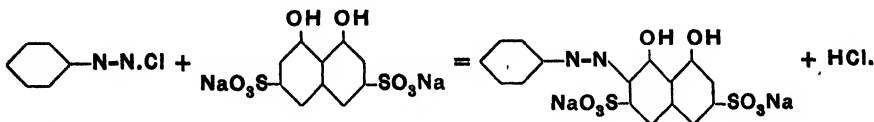


Alternatively,  $\alpha$ -amino-8-naphthol-3 : 6-disulphonic acid (H-acid) is heated with dilute sodium hydroxide under pressure.

Chromotropic acid is taken up by wool from a boiling acid bath, and becomes yellowish-brown on after-chroming, forming a chromium lake of 8-hydroxy- $\alpha$ -naphthoquinone-3 : 6-disulphonic acid,

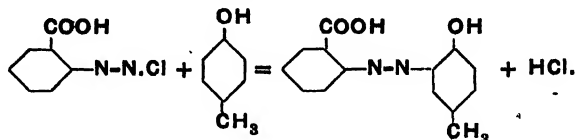


**Chromotrope Blue 2R (A.A.P.), XL Carmoisine 6R (B.D.C.)** (*After-chromed or acid mordant acid dyestuff*).—Diazobenzene chloride is coupled with chromotropic acid: 9.3 parts of aniline are diazotized, and the solution of diazobenzene chloride is run into a solution of 40 parts of chromotropic acid dissolved in water containing 15 parts of sodium hydroxide. The dyestuff separates gradually in a crystalline condition:



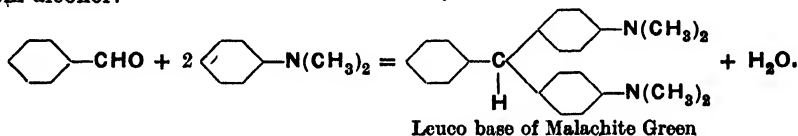
**Palatine Chrome Bordeaux B** (*after-chromed or acid mordant acid dyestuff*).—Diazotized anthranilic acid is coupled with *p*-cresol: 137 parts of anthranilic acid are diazotized, and added to a solution of 108 parts of *p*-cresol in 120 parts

of sodium-hydroxide solution (sp. gr. 1.38), keeping a slight excess of soda in the solution. After a few hours coupling is complete, and the dyestuff is precipitated completely by adding salt:

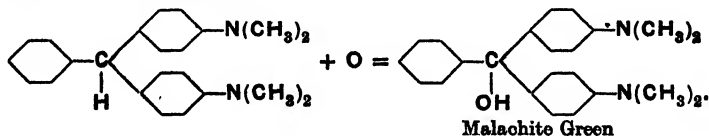


### Basic Dyestuffs.

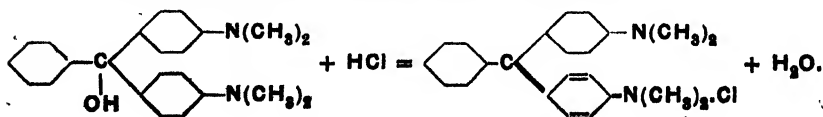
**Malachite Green** (*triphenylmethane derivative*).—Benzaldehyde,  $\text{C}_6\text{H}_5\text{CHO}$ , is condensed with dimethylaniline,  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ , in the presence of hydrochloric acid or sulphuric acid, and the leuco base of malachite green thus formed is oxidized with lead dioxide. A mixture of 45 g. of dimethylaniline, 30 g. of sulphuric acid (sp. gr. 1.84), and 15 g. of benzaldehyde is heated at  $100^\circ\text{C}$ ., with agitation, for twelve to fifteen hours, until condensation is complete. The mixture is then made slightly alkaline with sodium hydroxide, and excess of dimethylaniline is removed by distilling with steam. The residue after distillation is poured into an excess (about 1 litre) of cold water, and the mixture allowed to stand for some hours, till the leuco base separates. This is filtered off, washed with water, and dried at  $50^\circ\text{C}$ . It may be purified by crystallization from alcohol:



The leuco base is dissolved in 52 g. of hydrochloric acid (sp. gr. 1.16), 43 g. of acetic acid (sp. gr. 1.05), and 200 ml. of water. This solution is diluted with 800 ml. of water, cooled with ice to  $5^\circ\text{C}$ ., and oxidized with the theoretical quantity of freshly prepared lead-dioxide paste. The mixture is kept for from one to two hours, and the lead is then precipitated by adding a slight excess of Glauber salt, the lead sulphate being filtered off. The colour base is precipitated by adding ammonia. The precipitated base is filtered off, crystallized from brine, and dried at  $60^\circ\text{C}$ . To convert it into the oxalate, 40 g. are mixed with 16 g. of oxalic acid and 20 ml. of water, and stirred for two hours, after which 180 ml. of water is added, and the mixture is heated to  $70^\circ\text{C}$ . It is then filtered, a concentrated solution of 12 g. of oxalic acid added, and the solution allowed to crystallize:

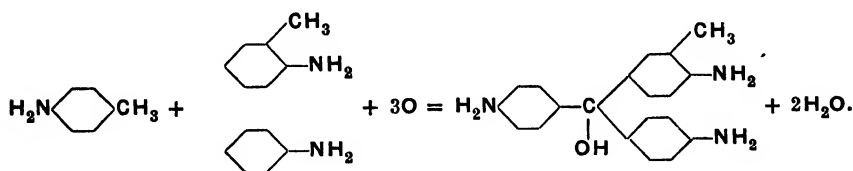


With hydrochloric acid, the hydrochloride is obtained:

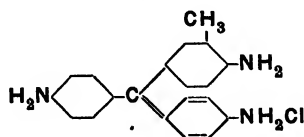


**Magenta, Rosaniline** (*triphenylmethane basic dyestuff*).—Equimolecular proportions of aniline, *o*-toluidine, and *p*-toluidine are oxidized with either nitrobenzene, arsenic acid, or mercuric nitrate. The *nitrobenzene process* is used commonly. For this, 20 parts of aniline, 80 parts of toluidine (containing 36 per cent. of *p*-toluidine), and 55 parts of nitrobenzene are used. Two-thirds of the mixture of aniline and toluidine (*aniline oil for red*) is introduced into an enamelled vessel, converted into hydrochlorides, and then dehydrated at 130° to 140° C. The remainder of the mixed amines and the nitrobenzene are then added, followed by from 2 to 3 per cent. of iron filings, and the mixture is heated with agitation. The melt is coloured violet at 120° C., but the formation of magenta begins only at 160° C. The temperature should not exceed 175° C., as at 190° C. the reaction is so violent that the dyestuff is destroyed. After heating at 175° C. for five hours, a sample is withdrawn, the heating being continued till the sample sets to a brittle mass on cooling. Steam is then passed into the mixture to remove any unchanged amines and nitrobenzene. The mass is then extracted with hot water containing hydrochloric acid and salt to remove iron chlorides and hydrochlorides of aniline and toluidine. The residue, which is a brittle mass with a green lustre, is extracted with boiling water under pressure, the insoluble by-products are allowed to settle, and the solution is filtered. Common salt is then added to precipitate the crude magenta, which is purified by repeated crystallization, with the addition of a little hydrochloric acid.

The nitrobenzene acts only indirectly as an oxidizing agent. Ferrous chloride is first produced by the action of the iron on hydrochloric acid. This is oxidized by the nitrobenzene to ferric chloride. The ferric chloride then oxidizes the amines, being at the same time reduced to ferrous chloride. The iron thus acts as an oxygen-carrier:



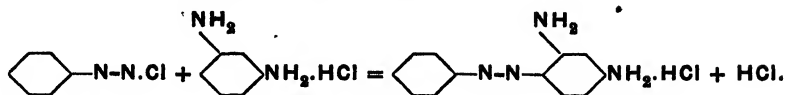
In presence of hydrochloric acid a chloride is formed having the formula:



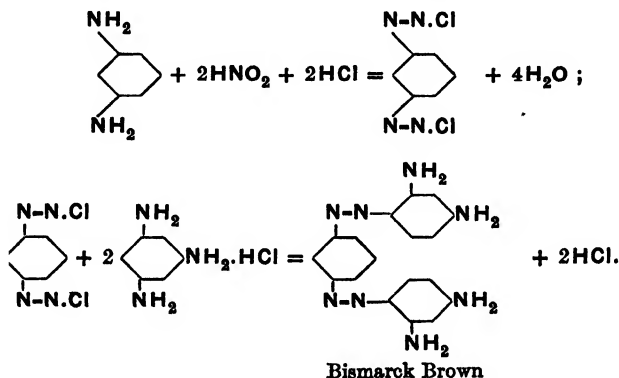
**Chrysoldine** (*monazo basic dyestuff*).—Twenty grams of aniline are dissolved in 63 g. of hydrochloric acid (sp. gr. 1.19) and 1.5 litres of water. Five hundred grams of ice are added, and then 14.8 g. of sodium nitrite dissolved in 500 ml. of water. The diazotized aniline solution is run into a solution of 25 g. of *m*-phenylenediamine in 250 ml. of 10 per cent. hydrochloric acid, the mixture is stirred, and a solution of sodium acetate is added until the liquid no longer gives an acid reaction to Congo Red. After all of the diazonium compound has been decomposed, the solution is boiled and filtered, and 250 g. of salt are added to the filtrate, which is then heated till the dye becomes crystalline.



The dyestuff is then filtered off, and dried:

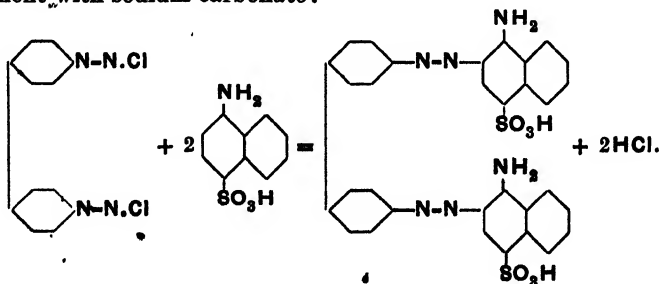


**Bismarek Brown** (*disazo basic dyestuff*).—This is made by the action of two molecular proportions of nitrous acid on three of *m*-phenylenediamine. A solution of 70 g. of sodium nitrite in 700 ml. of water is added to a very dilute solution of 145 g. of *m*-phenylenediamine hydrochloride; 370 g. of hydrochloric acid are then added at a temperature of 15° C., and the dyestuff is precipitated by the addition of salt. It is purified by dissolving it in water and salting out:

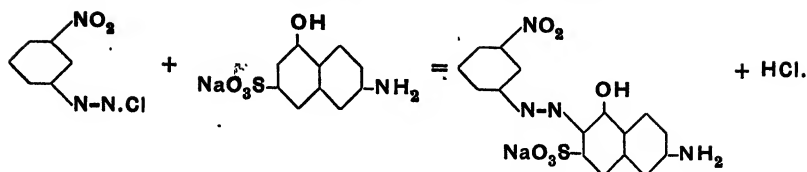


### Direct Dyestuffs.

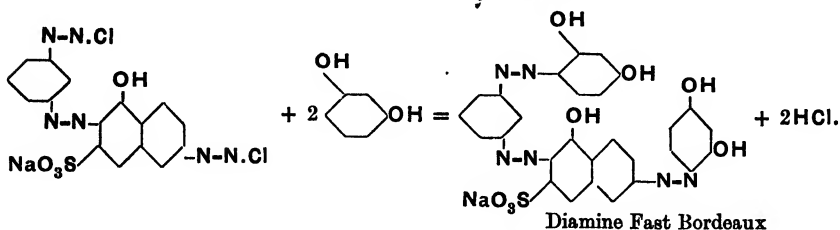
**Congo Red** (*disazo direct dyestuff*).—Tetrazotized benzidine is coupled with naphthionic acid (naphthylamine-4-sulphonic acid): 25.7 g. of benzidine hydrochloride are dissolved in 30 g. of hydrochloric acid (sp. gr. 1.19) and 500 ml. of water. A solution of 13.8 g. of sodium nitrite in 150 ml. of water is then added. The diazotized solution is then added to a solution of 55 g. of sodium naphthionate and 12 g. of sodium acetate in 1 litre of water. After twenty-four hours the mixture is filtered, and the dyestuff converted into the sodium salt by treatment with sodium carbonate:



**Diamine Fast Bordeaux** (*trisazo direct dyestuff*).—Metanitro-aniline is diazotized, and the product coupled with 2-amino-5-naphthol-7-sulphonic acid (J-acid) in alkaline solution:

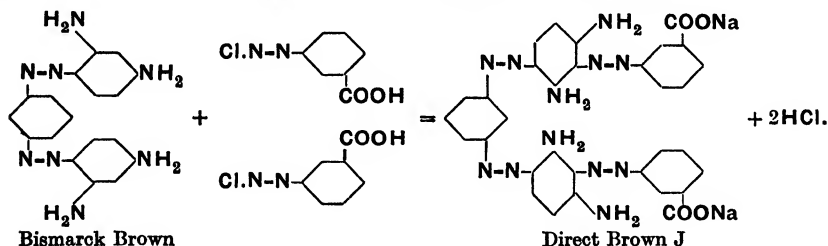


The nitro group is next reduced to an amino group, and this product then tetrazotized. This is coupled with two molecular proportions of resorcinol:



Alternatively, a solution of 38 parts of 2-*m*-aminobenzene-azo-6-amino-1-naphthol-3-sulphonic acid is treated with 70 parts of hydrochloric acid and 14 parts of sodium nitrite. This is then added to a solution of 22.5 parts of resorcinol in a slight excess of soda. The mixture is warmed, and the dye salted out.

**Direct Brown J (S.C.I.)** (*tetrakisazo direct dyestuff*).—Bismarck Brown is coupled with two molecular proportions of *m*-aminobenzoic acid:

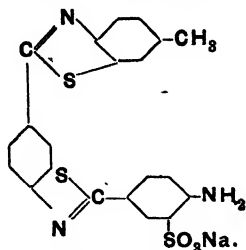


After mixing the solution of Bismarck Brown with the diazotized *m*-amino-benzoic acid and stirring, the solution is made alkaline, and the dyestuff (the sodium salt) is then salted out.

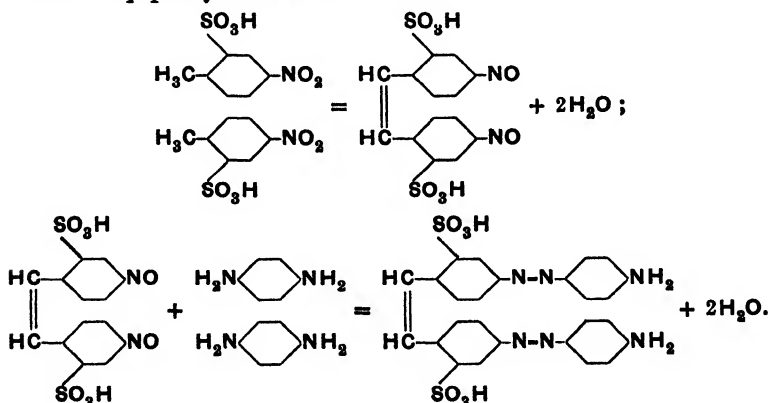
Benzo Brown B, Congo Brown, and Orion Brown are all similar dyestuffs, made from Bismarck Brown.

**Primuline** (*thiazole direct dyestuff*).—Two molecular proportions of *p*-toluidine are heated with  $4\frac{1}{2}$  atomic proportions of sulphur at  $200^{\circ}$  to  $280^{\circ}$  C., and the primuline base thus formed is sulphonated with fuming sulphuric acid (Green's process). A mixture of 100 parts of *p*-toluidine and 670 parts of sulphur is boiled with agitation for several hours, the temperature rising slowly as the reaction proceeds. Evolution of sulphuretted hydrogen commences at  $170^{\circ}$  C., and is completed when the temperature reaches  $270^{\circ}$  C. The product is blown out, cooled, and powdered. This is mixed with four times its weight of fuming sulphuric acid (30 per cent.  $\text{SO}_3$ ), and heated to  $70^{\circ}$  to  $80^{\circ}$  C. for a few minutes, till a little of the mixture dissolves in dilute alkali. The sulphonated mixture is then poured into cold water, and the precipitate which forms is filtered off. This consists of primuline-sulphonic acid together with

dehydrothio-*p*-toluidine-sulphonic acid. The mixture is stirred with cold concentrated ammonia. The primuline-sulphonic acid dissolves, while the ammonium salt of dehydrothio-*p*-toluidine-sulphonic acid crystallizes out. The latter is filtered off, and washed with a little water till almost white; the Primuline is then salted out of the filtrate, its formula being

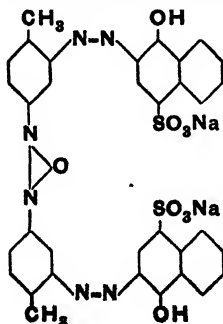


**Cotton Brown R (Gy.)** (*stilbene direct dyestuff*) is made by condensing equimolecular proportions of *p*-nitrotoluene-*o*-sulphonic acid and *p*-phenylenediamine in the presence of concentrated aqueous sodium hydroxide. Sixteen kilograms of *p*-nitrotoluene-*o*-sulphonic acid and 8 kg. of *p*-phenylenediamine are dissolved in 50 litres of boiling water, and 12 kg. of sodium hydroxide solution of sp. gr. 1.384 are added. After a short time the mixture boils vigorously, and when the reaction is complete the dyestuff is salted out. Dinitroso-stilbene-disulphonic acid is apparently first formed, and this condenses with the *p*-phenylenediamine:



It is of interest to note that an azo group is formed here by condensation.

**Rosophenine:**



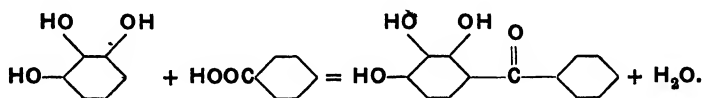
**Rosophenine 4B** (*azoxy direct dyestuff*).—This dye is derived from diamino-azoxytoluene, which is tetrazotized with nitrous acid in the presence of hydrochloric acid. The product is then coupled with two molecular proportions of 1 : 4-naphtholsulphonic acid (NW-acid): see formula at foot of page 522.

### Sulphur Dyestuffs.

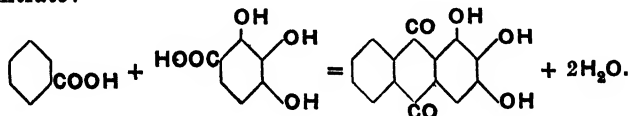
**Autogene Black EEB**.—A solution of 30 g. of sulphur, 40 g. of sodium sulphide (62 per cent.), and 40 ml. of water is added in small portions at a time to a boiling solution of 33.5 g. of the sodium salt of 2 : 4-dinitrophenol in 80 ml. of water. The temperature of the boiling mixture is raised to 106°–108° C. by the addition of salt or sodium sulphate. Boiling is continued under a reflux condenser for from ten to fifteen hours. After dilution, the dye is filtered off and washed.

### Mordant Dyestuffs.

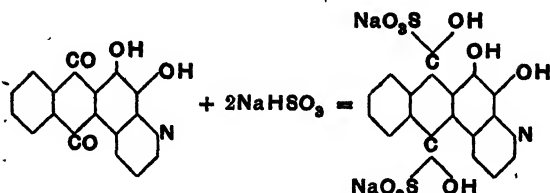
**Alizarine Yellow A** (1 : 2 : 3-*trihydroxy-benzophenone*).—Pyrogallol is condensed with benzoic acid in the presence of zinc chloride: Fifty parts of pyrogallol and 50 parts of benzoic acid are heated to 145° C., and 150 parts of anhydrous zinc chloride are added gradually with stirring. After about three hours a sample dissolved in hot water should deposit no benzoic acid on cooling, but only crystals of the dyestuff. The melt is then dissolved in 300 parts of boiling water, boiled for two hours with the addition of animal charcoal, and filtered. The product crystallizes out in light-yellow needles on cooling:



**Anthracene Brown OB** (1 : 2 : 3-*trihydroxy-anthraquinone*).—Pure gallic acid is heated with benzoic acid and sulphuric acid. 36.6 parts of pure benzoic acid are stirred with 300 parts of 100 per cent. sulphuric acid until dissolved, and the solution is heated slowly to 90° C. Fifty parts of pure gallic acid, dried at 110° C., are added in small portions during one hour, and the mixture is then heated at 118° C. for six hours. The product is poured carefully into 1000 parts of boiling water with stirring, and filtered whilst hot. The residue is washed till free from acid, the excess of benzoic acid crystallizing from the filtrate:

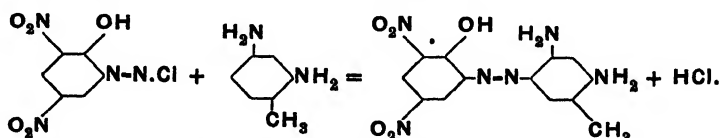


**Alizarine Blue S** (*soluble mordant dyestuff: the sodium bisulphite compound of alizarine blue*).—A 10 to 20 per cent. aqueous paste of alizarine blue is stirred with 25 to 30 per cent. of sodium bisulphite solution of sp. gr. 1.25, and the mixture is kept for from eight to fourteen days, air being excluded. It is then filtered from unaltered alizarine blue, and the filtrate is precipitated with salt or evaporated at a low temperature:

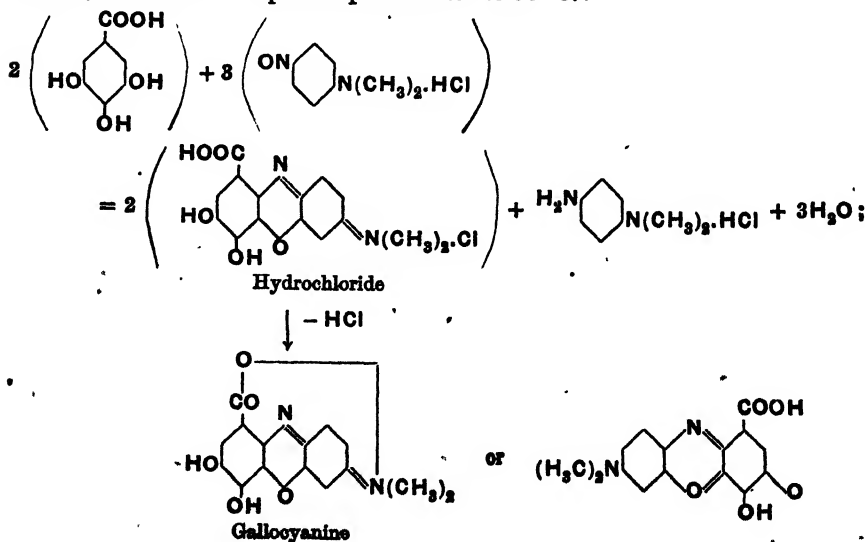


The product is yellowish-brown, giving a solution in water which decomposes when heated above  $70^\circ \text{C.}$ , with precipitation of alizarine blue.

**Metachrome Brown B (A.A.C.), Alizarine Brown M Paste (B.D.C.).**—Picramic acid is diazotized, and coupled with *m*-phenylenediamine, *m*-toluylenediamine, or chloro-*m*-phenylenediamine: 22.1 parts of the sodium salt of picramic acid are dissolved in water, and diazotized with 20 parts of hydrochloric acid (sp. gr. 1.16) and 6.9 parts of sodium nitrite. The solution of the diazo compound is added to an aqueous solution of 12.2 parts of 1:3-toluylenediamine. The mixture is stirred for several hours, and 5.3 parts of sodium hydroxide are then added. The mixture is warmed, and the dyestuff salted out:



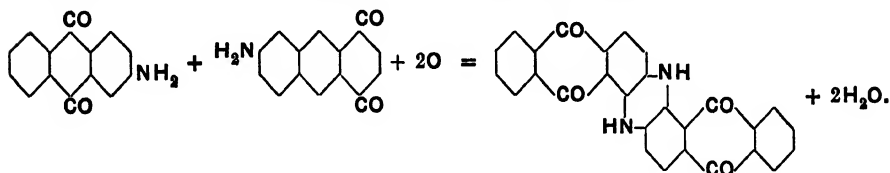
**Gallocyanine (oxazine basic mordant dyestuff).**—Gallic acid, dissolved in methyl alcohol, is treated with excess of *p*-nitroso-dimethylaniline hydrochloride: A mixture of 75 parts of gallic acid, 35 parts of *p*-nitroso-dimethylaniline hydrochloride, and 850 parts of methyl alcohol is boiled under a reflux condenser, and a further 85 parts of *p*-nitroso-dimethylaniline hydrochloride are added, gradually, during four hours. Boiling is continued till a drop of the mixture, when placed on a filter-paper, gives a deep violet spot, without a yellow rim. The alcohol is then distilled off, the residue boiled with water, filtered, and dried on a porous plate at  $40^\circ$  to  $50^\circ \text{C.}$ :



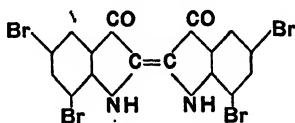
## Vat Dyestuffs.

**Duranthrene Blue RD Extra Paste (B.D.C.).**— $\beta$ -Amino-anthraquinone is heated with potassium hydroxide in the presence of potassium nitrate.

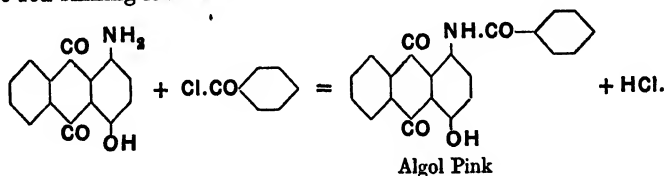
Ten parts of  $\beta$ -amino-anthraquinone, 20 to 50 of potassium hydroxide, and 2 of potassium nitrate are heated to 200° C. The temperature is then raised to 250° C. for half an hour. The product is poured into water, boiled, and filtered. The crude duranthrene blue is purified by treating it with sodium hydrosulphite and sodium hydroxide, whereby the soluble leuco compound is formed. This is then re-oxidized by means of a current of air:



**Durindone Blue 4B Paste (B.D.C.)** (5 : 7 : 5' : 7'-*tetrabromindigo*).—Sixteen to eighteen parts of bromine are added to a suspension of five parts of indigo in 50 parts of nitrobenzene, and the mixture is heated gradually to 225° C. during one and a half hours under a reflux condenser, and then boiled gently for a further one and a half hours. After cooling, the violet crystalline product is filtered off, and washed with alcohol:



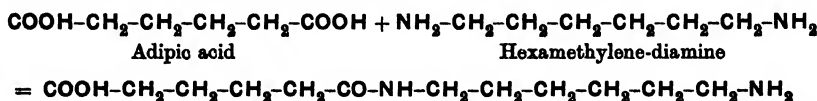
**Algol Pink R Paste.**—Ten parts of 1-amino-4-hydroxy-anthraquinone, 100 parts of nitrobenzene, and 20 parts of benzoyl chloride are boiled together for about half an hour. The mixture is cooled, and the dyestuff crystallizes in bronze-red shining leaflets:



## ADDENDA.

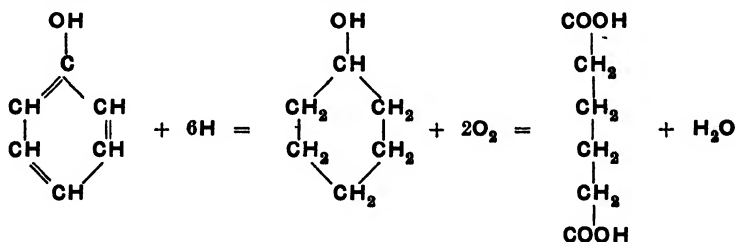
Add to page 138:—

**Nylon** is a generic name applied to threads made from super-polyamides. These polyamides are prepared by condensation of amides with carboxylic acids. The nylon thread which has been manufactured in bulk is obtained by the condensation of adipic acid with hexamethylene-diamine:—



The carboxyl and amino groups at the ends of the condensate in the above equation are free to unite with further molecules of adipic acid and hexamethylene-diamine. In this way a long-chain molecule of a polymeride capable of being drawn out into a continuous thread is produced.

The starting-point in the sequence of reactions resulting in nylon is phenol. The phenol is reduced to cyclohexanol and then oxidized to adipic acid:—



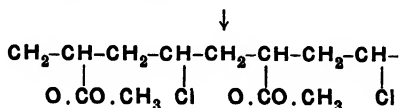
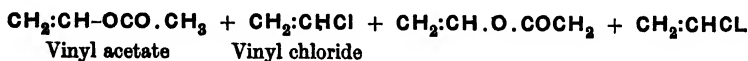
A portion of the adipic acid is retained and a part is heated with ammonia under pressure, when it becomes converted to hexamethylene-diamine.

When a solution containing the appropriate quantities of adipic acid and hexamethylene-diamine is heated in an enclosed vessel at 200° C. under a pressure of 250 lbs., a thick syrupy mass of nylon polymer, which solidifies on cooling, settles out at the bottom of the tank. When a slit is opened, the pressure inside the vessel forces the polymer out in the form of a ribbon, which is solidified by passing over an internally water-cooled drum. This ribbon is broken up into chips which constitute the raw material out of which the yarn is spun. The polymer chips are molten in an atmosphere of nitrogen, and the melt is extruded through fine nozzles, when, on cooling, it solidifies into a continuous thread.

Nylon possesses an extremely high tensile strength and, what is more important, it does not lose this when wet. The tensile strength is about 5 g. per denier dry and 4.5 g. per denier wet. The corresponding figures for pure silk are 4.6 g. dry and 3.8 g. wet. Nylon also possesses a very high degree of elastic recovery.

An important and unique property of nylon is that a permanent set can be imparted to it in boiling water or by the action of steam under pressure. Thus, if a seamless stocking be pulled onto a shaped board and treated with steam under pressure for a few minutes, the shape imparted is permanent, so long as the stocking is never subjected to a temperature higher than that used in the setting operation.

**Vinyon** is produced by the co-polymerization of vinyl chloride and vinyl acetate:—



This co-polymer is dissolved in acetone, and when the solution is of the right viscosity it is forced through spinnerets into a hot-air chamber, where the acetone is evaporated, leaving the vinyon thread. Vinyon has a melting-point of 65° C., which renders it unsuitable for textile purposes, but on account of its high degree of resistance to acid and alkali it finds an outlet for the manufacture of filter cloths for chemical manufacturing processes. A recent product known as Vinyon E has a softening-point of about 120° C. and possesses a very high degree of elasticity.

Add to page 186, before "Properties of Chlorinated Wool":—

**Recent Unshrinkable Finishes.**—During recent years much attention has been devoted to improving the methods of making wool resistant to shrinkage. The Wool Industries Research Association has investigated the use of enzymes. *Papain* is an enzyme obtained from the juice of the paw-paw fruit, and when dissolved in sodium bisulphite solution can bring about partial degradation of the wool scales, thus preventing shrinkage. Practically all chemicals which reduce the felting power of wool cause degradation of the protein molecule, generally by attacking the cystine linkages. Degradation of the tips of the scales is a significant factor in producing unshrinkability, but any attack on the cystine in the cortex is causing damage to the wool without playing any essential part in promoting resistance to felting. It is, therefore, desirable to restrict the action to the surface of the fibre, and it is claimed that the complex molecules of the enzyme are too large to penetrate into the cortex, only the scales being accessible to them.

Alkalis have also been used to attack the sulphur linkages. Obviously aqueous solutions cannot be used because the degree of degradation of the keratin cannot be controlled. When alkalis are dissolved in organic solvents, however, the reaction is controlled and confined to the surface of the fibre, and a high degree of unshrinkability can then be produced. In the Ferney and Lipson process, wool is treated with caustic soda or potash dissolved in methylated spirit. The use of inorganic sulphides dissolved in methylated spirit or other of the lower alcohols has been described by Parker, Farrington, Stubbs and Speakman. Another variation of the use of alkalis has been patented by Hall, Wood, and Tootal, Broadhurst Lee; they use white spirit, which is probably the cheapest organic solvent available as the medium in which the reaction can be carried out. Caustic soda is not soluble in the solvent, but this difficulty is overcome by the addition of *n*-butyl alcohol. In



all processes in which alkalis are applied in organic solvents the moisture content of the wool is critical, and the material must be dried to a pre-determined state before the treatment is carried out.

The Negafel process, which has been patented by Clayton and Edwards, consists of treating wool with chlorine produced in aqueous solution by the action of formic acid on alkali hypochlorites. The reaction is carried out at a pH between 4 and 5, because under such conditions the degree of swelling of the fibre is at a minimum and penetration of chlorine into the cortex is restricted. Another important feature of this process is careful attention to the pH of the scouring liquor, in order to ensure that the wool does not enter the chlorinating bath in a swollen state.

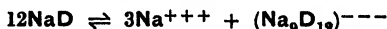
Add to page 359, before "Special Methods":—

**High-Temperature Method of Dyeing.**—During recent years a new technique has been developed which gives very successful results with many of the neutral-dyeing acid dyes—a group which is generally very unlevel-dyeing. Acid dyes which only develop an affinity for wool at a low pH are considered to be completely ionized in solution. If D represents the dye acid portion of the molecule, the ionization proceeds thus:—



Such dyes give level shades when applied from acid liquors, and the best results are obtained by entering at a low temperature and raising to the boil gradually.

The neutral-dyeing dyes form aggregate ions according to the following equation:—



The more complex the aggregate the greater is the tendency towards unlevel dyeing. The aggregates become less complex at higher temperatures, and it has been found that with unlevel-dyeing acid dyes better results are obtained if the goods are entered just under the boil. In the same way, assistants such as Glauber's salt increase aggregation and should not be used with neutral-dyeing acid dyes which are difficult to level.

In the method of dyeing described by Goodall, the bath is made up without Glauber's salt but with ammonia or ammonium sulphate in addition to the dyestuff. The liquor is raised to the boil and the steam is turned off. The goods are then entered and the liquor raised to the boil again and maintained at this temperature until exhaustion is complete (Goodall, *J. Soc. Dyers Col.*, 1938, page 45).

Add to page 386, before "Standing Baths":—

**Rate of Dyeing.**—Direct cotton dyes vary greatly in the rates at which they are taken up by cotton or other cellulosic fibres. The importance of this was first recognized by Boulton and Reading (see page 467, above) in connection with the dyeing of rayon; and they use the "time of half-dyeing" test as a measure of rate of exhaustion. Information about the rate of exhaustion is also significant in dyeing cotton. Dyes with similar rates of exhaustion are compatible. The shade will therefore be built up uniformly as the dyeing proceeds with mixtures of compatible dyes, and this will make matching easier. When, however, dyes with appreciable differences in exhaustion properties of "times of half-dyeing" are used together, one component will

be taken up before the other, and there will be a marked change in the shade of the material during the course of the dyeing. Apart from the "time of half-dyeing," rates of exhaustion can be plotted as curves. The usual procedure is to prepare seven dyebaths of standard composition and to dye seven hanks at a uniform temperature during periods of 1½, 3, 5, 7, 15, 30 and 60 minutes. The amount of dyestuff absorbed is determined either by comparing the hanks with standard dyeings or by a colorimetric examination of the liquors. From the information acquired in this matter a curve can be plotted graduating time on one axis and percentage exhaustion on the other.

**Migration Properties.**—The rate of migration has an important bearing on the level-dyeing property of the colour. Many dyes "strike," or are absorbed, in the first instance, extremely rapidly and far from uniformly throughout the piece. If the migration properties are good, this initial unlevelness is no disadvantage because after a short interval there is a redistribution, and uniformity is achieved. When, however, there is a low rate of migration, a rapid "strike" will lead to unlevel dyeing.

To assess migration, 2 per cent. dyeings of the dyestuff are boiled in water containing 10 per cent. of Glauber's salt on the weight of the cotton, together with bleached hanks of equal weight, during periods of 15, 30, 45, 60, 90, 120 and 240 minutes. The amount of dyestuff transferred from the original hank is ascertained by comparison of the shade of the bleached hank with a series of standards, and also by taking into account the amount of dyestuff transferred to the liquor, which may be estimated colorimetrically. From this information migration curves may be constructed.

Add to page 476, before "Azoic Colours":—

**Dyeing Nylon.**—At present there is very little practical experience in dyeing nylon in this country. One important factor to be taken into account is that if the goods contain any creases before they enter the dyebath the marks will become permanent after dyeing. In order to avoid this defect the goods are either "pre-boarded" or pre-set before dyeing. Garments, including stockings, are pre-boarded by pulling them onto a metal board or shape which applies sufficient tension to remove all the creases, and they are then heated during about five minutes in a sealed chest with steam at about 5 lbs. per square inch pressure. This process not only removes creases but also imposes a shape which is permanent so long as the garments are never subsequently subjected to a temperature higher than that of pre-boarding. Since the temperature of steam at 5 lbs. pressure is higher than that of boiling water, it can be assumed that the shape will be permanent to ordinary dyeing and washing methods. Pre-setting is applied to piece-goods where it is only necessary to remove creases and it is not desired to impose a shape; thus no board is used, but the goods are only treated with steam under pressure, with an appropriate uniform degree of tension.

**Dyeing Nylon with Dispersed Colours.**—Nylon possesses an affinity for dispersed acetate dyes. It is recommended that the temperature should be maintained at 85° to 90° C., and that soap should be added to the dyebath. Where penetration presents difficulties, however, such as in the dyeing of seams in stockings, it may be necessary to raise the temperature to the boil. The dispersed colours give a good degree of levelness and are particularly successful in covering up variations in the yarn. They give dyeings of good fastness to washing and fair fastness to light.

**Acid Dyes.**—Nylon can also be dyed with many acid dyes from neutral or acid liquors. Generally speaking, the presence or absence of acid is governed

by the conditions required for dyeing wool with the same dyestuffs. The acid dyes are of better fastness to light than dispersed colours, but they are more prone to show up variations in yarn or texture. Care should also be taken in selection of dyes because the rates of exhaustion show great variations on this fibre.

## INDEX.

- ABIETIC acid**, 199  
**Acetic acid**, 214  
**Acetyl rayon**, 135  
 —, dyeing of, 469  
 —, faults in dyed, 476  
**Acids**, 207  
**Acid dyestuffs**, 349, 515  
 —, application to cotton, 364  
 —, — silk, 364  
 —, — wool, 356  
 —, assistants used, 352  
 —, fastness of, 356  
 —, function of acid used with, 352  
 —, Glauber salt used with, 354  
 —, identification of, 496  
 —, preparation of, 515  
 —, properties of, 351  
 —, special methods of dyeing, 358  
 —, subdivisions of, 355  
 —, types of, 349  
**Acid chrome dyestuffs**, 361  
 —, —, method of dyeing, 362  
 — mordant dyestuffs, 361, 417  
 —, —, identification of, 496  
 — Yellow, preparation of, 515  
 — Magenta, preparation of, 516  
**Adsorption**, 41  
**Air as a bleaching agent**, 243  
**Aktivin**, 463  
**Algin**, 327  
**Algol colours**, 454, 468, 525  
**Alizarine**, 439  
 —, application to cotton, 441  
 —, — wool, 440  
 — Blue, preparation of, 523  
 — Yellow, preparation of, 523  
**Alkalis**, 207  
**Aluminium acetate**, 206  
**Ammonia**, 210  
**Ammonium acetate**, 359  
**Aniline**, 4  
 — Black, 442  
 —, —, aged, 445  
 —, —, detection of, on cotton, 447  
 —, —, dyeing, methods of, 443  
 —, —, identification of, 497  
 —, —, steamed, 447  
**Animal fibres**, tests for, 65  
**Anthracene**, 4  
 — Brown, preparation of, 523  
**Anthraquinone vat dyestuffs**, 453, 458  
**Antiseptics**, 37, 330  
**Anthrax**, 162  
**Aqua regia**, 221  
**Artificial vegetable fibres**, 66  
 —, —, bleaching of, 463  
 —, —, dyeing of, 464  
**Autogene Black**, preparation of, 523  
**Auxochromes**, 9  
**Azines**, 503  
**Azo compounds**, 6  
**Azoic colours**, 400, 403  
 —, identification of, 497  
 —, — on wool, silk or union base, 408  
 —, — on rayon goods, 476  
**Azophor Orange**, 403  
  
**BACILLI**, 32  
**Bacteria**, 32  
**Barium sulphate**, 329  
**"Barriness,"** 465  
**Basic dyestuffs**, 368  
 —, application to artificial fibres, 464, 469  
 —, — cotton, 377, 380  
 —, — silk, 374  
 —, — wool, 376  
 —, identification of, 496  
 —, properties of, 371  
 —, theory of dyeing with, 373  
 —, uses of, 373  
**Basic mordant dyestuffs**, 417  
**Bast soap**, 145  
**Beetling**, 311  
**Benzene (benzole)**, 247  
**Benzine**, 246  
**Bismarck Brown**, 371, 500  
 —, preparation of, 520  
**Bleaching agents**, 216  
 —, non-chlorinated, 234  
 —, defects of cotton goods due to, 305  
**Bleaching powder**, 227  
 —, analysis of, 230  
 —, use in bleaching, 232  
**Blueing agents**, 332  
**Bonsor's Black**, 427  
**Borax**, 209  
**Boric acid**, 331  
**Bromination of wool**, 185  
**Brownian movement**, 198  
**Bursting test for fabrics**, 86  
  
**CALCIUM sulphate**, 329  
**Caledon colours**, 454  
**Calendering**, 312  
**Carbon tetrachloride**, 247  
**Carminic acid**, 437  
**Carnauba wax**, 328  
**Casein fibres**, 66, 136

- \* Catechu, 436
  - Caustic potash, 207
  - soda, 207
  - Cellulose, 105
    - acetate rayon, 135
    - nitrate, 129
    - peroxide, 108
    - , physical and chemical properties of, 110
  - Cellutyl colours, 469
  - Ceresin, 330
  - Chardonnay rayon, 129
  - Cheese-dyeing machines, 340
  - China clay, 329
  - Chlorazol dyestuffs, 464, 480, 484, 486
  - Chloride of lime, 227
  - Chlorination of wool, 181
  - Chlorine, action on wool, 183
    - , as bleaching agent, 220
  - Chrome Yellow, 460
  - Chromium oxides as mordants, 419
  - Chromogens, 9
  - Chromophores, 8
  - Chromotrope dyes, 361
    - Blue, preparation of, 517
  - Chromotropic acid, 517
  - Chrysoidine, preparation of, 519
  - Ciba dyes, 453
  - Coal tar, 2
  - Cocci, 32
  - Cochineal, 437
  - Colloids, 32, 40, 197, 198
  - Colorimeters, 27
  - Colour-matching, 487, 491
    - — by synthesis, 493
    - , measurement of, 27
    - , theory of, 487
  - Coloured cotton goods, bleaching of, 304
  - Complementary colours, 489
  - Condition weight of textiles, 70, 72
  - Congo Red, 381
    - —, preparation of, 520
    - — test, 306, 307
  - Cotton, 90
    - , amidated, 121
    - , bleached, tests for, 304
    - , bleaching of, 285
    - , — — coloured goods, 304
    - cellulose, *see below*
    - , classification of, 93
    - , constituents of, 99
    - , count of yarns, 74
    - , damage due to bleaching, 305
    - , finishing, 308, 333
    - , grades of, 94
    - , immunized, 121
    - , lye boiling, 289, 292
    - , — — with organic solvents, 295
    - , mercerized, 117
    - , mineral matter in, 105
    - oils and waxes, 99
    - , schreinerized, 120
    - spinning, 92
    - , structure of, 95
  - Cotton Brown R, 382, 522
  - Cotton cellulose, 105
    - —, special properties of, 110
  - Cotton cellulose, action of acids on, 112\*
    - —, — — air on, 110
    - —, — — alkalis on, 115
    - —, — — micro-organisms on, 111
  - Cotton-silk mixtures, dyeing of, 481
  - Cotton-wool mixtures, dyeing of, 478
  - Count of spun yarn, 74
    - , conversion of, 77
    - , true, 76
  - Coupled colours, 397
  - Coupling bath, 399
    - —, using diazotized bases, 406-7
  - Cuprammonium rayon, 132
  - Curd soaps, 201
  - Cutch, 436
  - Cystine, 167, 527
- DAMAGE and defects in dyed goods, 510**
- Decrolein, 220
  - Delustring, 477
  - Developers, 392
  - Dextrins, 323
  - Diamine Fast Bordeaux, 382, 520
  - Dianisidine Blue, 403
  - Diazotization, 391, 393, 473
  - Direct Brown, preparation of, 521
  - Direct dyestuffs, 361
    - —, after-treatment of, 387
    - —, analysis of, 504
    - —, application to cotton, 386
    - —, — — regenerated cellulose rayons, 464
    - —, — — silk, 390
    - —, — — wool, 389
    - —, assistants used with, 384
    - —, chemical nature of, 381
    - —, conditions for dyeing, 385
    - —, developed colours, 391
    - —, properties of, 382
    - —, theories of dyeing with, 383
  - Disinfectants, 37
  - Dispersed dyestuffs, 474
  - Duranol colours, 474-5
  - Duranthrene Blue, preparation of, 525
  - Durindone colours, 457
    - Blue, preparation of, 525
  - Dyeing, general conditions of, 11
    - , history of, 1
    - machines, 237
    - , rate of, 528
    - , theories of, 42
  - Dyestuffs, analysis of, 502
    - , classification of, 10
    - , commercial, 10
    - , —, analysis of, 504
    - , dispersed, 474
    - , identification of, 496, 499
    - , migration of, 529
    - , nomenclature of, 10
    - , preparation of, 7, 513
    - , separation of, 500
    - , tests of dyeing values of, 508
- EAU DE JAVELLE, 223**
- Electrolytic bleaching apparatus, 224
  - Emulsification process (wool scouring), 267
  - Emulsions, 41, 196

**Enzymes**, preparation of, 38  
 —, properties of, 37  
 —, uses of, 38, 322  
**Eosine dyes**, 359, 365  
**Equalizing power**, test of, 509  
**Exhausting powers of dyestuffs**, 508, 528

**FASTNESS** of dyestuffs, tests for, 366

**Fats**, 190

**Fatty acids**, 191

**Fibroin**, 147

**Filling materials**, 329

**Finishes**, cotton, 308, 311

—, —, assisted and stiffened, 317

**Finishing mixtures (cotton)**, 333

**Fireproofing agents**, 332

**Flash-point of oils**, 275

**Flavine**, 435

**Flax**, 122

**Formaldehyde**, 330

—, action on starch, 322

**Formic acid**, 214

**Formosols**, 220

**French chalk**, 329

**Fustic**, 433

**GALLOCYANINE**, preparation of, 524

**Gelatin and glue**, 325

— — —, analysis of, 327

**Glauber's salt**, 330, 385

**Glycerin (Glycerol)**, 190

**Green's method of analysis of dyestuffs**, 502

**Gum arabic**, 328

— **tragacanth**, 328

— **tragasol**, 328

**Gypsum**, 329

**HAIR**, 163

—, difference from wool, 157

**Half-dyeing test for direct dyes**, 467, 528

**Hardness in water**, 49

— — —, removal of, 53

**Hemp**, 126

**Hexalin**, 249

**Hexamethylene-diamine**, 526

— **tetramine**, 322, 331

**High-temperature dyeing**, 528

**Humidity**, 68

—, determination of, 68

**Hydrocarbons as solvents**, 246

—, chlorinated, 247

**Hydrocellulose**, 106

**Hydrochloric acid**, 211

— —, specific gravity data for, 213

**Hydrogen-ion concentration**, 14

— — —, determination of, 16

**Hydrogen peroxide**, 234

— —, detection and estimation of, 237

— —, properties of, 235

**Hydrogenated hydrocarbons**, 249

— **phenols**, 249

**Hypochlorous acid**, 221

**IONLAND moss**, 328

**Indamine Blue**, 370

**Indanthrene dyes**, 454, 468

**Indicators**, 16

**Indigo**, 449 ff.

—, application of, 455

—, estimation of, 459

—, synthesis of, 452

— **White**, 451

**Indigoids**, 449

**Indigosols**, 458

**Indigotin**, 450

**Indirubine**, 451

**Induline Scarlet**, 370

**Insoluble azoic colours**, 400

**Intermediates**, 4

**Ionamine dyestuffs**, 471

— —, application of, 473, 486

**Ionization**, 13

**Irish moss**, 328

**Iron Buff**, 461

**Isatin**, 451

**JANUS dyestuffs**, 371, 481

**Japan wax**, 330

**Jute**, 127

**KAOLIN**, 329

—, use of, in separation of dyestuffs, 501

**Katanol**, 379

**Keirs**, 290

**Kemps**, 163

**Keratin**, 116

**Kermes**, 438

**Khaki**, mineral, 461

**Kiton Red process for estimation of damage to wool**, 175, 188

**LAC**, 438

**Lanital**, 136

**Lea**, 81

**Lignocellulose**, 105

**Lime boiling**, 294

**Logwood dyes**, 424 ff.

— **Black**, 426

—, detection of, 426

—, dyeing with, 425

— on cotton, 428

— — **silk**, 429

— — **wool**, 426

**Lye boiling of cotton**, 289

**Lyons Black**, 430

**MAOLURIN**, 434

**Madder**, 438

**Magenta**, preparation of, 519

**Magnesium carbonate**, 49

— **sulphate**, 49, 330

**Malachite Green**, 368, 377

— —, preparation of, 518

**Manganese Brown**, 461

**Meldola's Blue**, 369

**Mercerized cotton**, 117

— —, tests for, 120

**Merino**, 164

**Metachrome dyestuffs**, 362, 417

— **Brown**, preparation of, 524

**Meta-nitro-aniline Orange**, 403

**Methyl Green**, 368

- Methylene Blue**, 369  
**Methylhexalin**, 249  
**Micro-organisms**, 32  
 —, causes of infection, 36  
 —, inhibiting growth of, 37  
 —, products of growth of, 36  
**Microscopes**, 22  
**Mineral pigments**, 460  
**Mixed dyestuffs**, testing for, 498  
 — —, separating, 500  
 — fibres, dyeing of, 363, 478  
 — —, — —, containing regenerated cellulose, 485  
 — —, — —, — cellulose acetate, 485  
 — —, regain of, calculating, 72  
**Moisture content of textile fibres**, 67, 69  
 — — — —, determination of, 71  
**Monochrome colours**, 362  
**Mordants**, 419  
**Mordant dyestuffs**, 416  
 — —, dyeing with, 418, 423  
 — —, identification of, 497  
**Mordanting cotton**, 421  
 — silk, 423  
 — wool, 419  
**Morin**, 433  
**Mottled soaps**, 201  
**Moulds**, 34  
**Multicellular fibres**, 122  
**Mungo**, 165
- NAPHTHALENE**, 4  
**Naphthol**, 4  
 — colours, 400  
 — -AS colours, 403  
 — — —, method of dyeing, 404  
 — Yellow S, preparation of, 515  
**Naphthylamines**, 403  
**Neatsfoot oil**, 193  
**Neolan dyestuffs**, 363  
 — —, method of dyeing, 363  
**Nepe**, 98  
**Nitro-aniline**, 397  
**Nitro rayon**, 66, 129  
**Nitrosamine Red**, 398, 402  
**Nylon**, 526  
 —, dyeing, 529
- OIL**, determination of, in fabrics, 88  
**Oils**, 190  
 —, flash-point of, 295  
 —, lubricating, for wool, 274  
 —, rancidity of, 192  
 —, sulphonated, 199  
 —, textile, 192  
**Oil soaps**, 201  
**Olive oil**, 192  
**Orange II**, preparation of, 516  
**Organic solvents**, 246  
**Oxalic acid**, 214  
**Oxycellulose**, 107, 108  
**Ozone**, 243
- PALATINE Chrome Bordeaux**, preparation of, 517  
**Paranil A**, 398
- Para-nitro-aniline**, 397  
 — Red, 400  
**Pattern dyeing**, 478, 492  
**Pectins and pectoses of cotton**, 104  
**Perborates**, 249  
**Perilene dyestuffs**, 454  
**Permutit**, 59  
**Peroxide of hydrogen**, 234  
**Persulphates**, 240  
**Petroleum spirit**, 246  
 — jelly, 330  
**Phenylene Blue**, 369  
**Phthaleins**, 359  
**Pink salt**, 150, 431  
**Potassium dichromate**, 242  
 — hydroxide, 207  
 — permanganate, as oxidizing agent, 240  
 — persulphate, 240  
**Primuline**, 382, 391  
 —, developers for, 392  
 —, preparation of, 521  
**Proteins of cotton fibre**, 100  
**Prussian Blue**, 462  
**Purpurine**, 439
- QUERCITRON**, 435  
 —, dyeing with, 436
- RAMIE**, 125  
**Rancidity of liquid oils**, 191  
 — of soaps, 192  
**Rayon (artificial silk)**, 129  
 —, acetyl, 135  
 —, —, dyeing, 469  
 —, —, —, saponification method, 470  
 —, bleaching of, 464  
 —, chardonnet, 129  
 —, cuprammonium, 132  
 —, non-creasing, 477  
 —, preliminary treatment of, 463  
 —, regenerated cellulose, dyeing of, 464  
 —, — —, — —, with direct dyestuffs, 464  
 —, — —, — —, — vat dyestuffs, 468  
 —, scouring, bleaching and dyeing of, 463  
 —, special effects on, 477  
 —, staple fibre, 135  
 —, viscose, 133  
**Regains**, 70  
**Resorcin Brown**, preparation of, 517  
**Rhodamines**, 370, 500  
**Rhoduline Violet**, 370  
**Ricinoleic acid**, 199  
**Ricinosulphuric acid**, 199  
**Rosaniline**, preparation of, 519  
**Rosin soap**, 198  
**Rosophenine**, 382, 523
- SAFRANINE**, 370  
**Salicylic acid**, 331  
**Salmon Red**, 381  
**Scroop**, 214, 477  
**See silk**, 152  
**Separation of dyes**, 500  
**Sericoil**, 145  
**Serioculture**, 140  
**Shrinkage of chlorinated wool**, tests of, 189

- Silk, 139  
   —, Byssus, 152  
   —, éceru, 146  
   —, souple, 146  
   —, spider, 152  
   —, Tussur, 151  
   —, wild, 150  
 Silk, action of acids on, 148  
   —, — — alkalis on, 149  
   —, — — boiling water on, 363  
   —, — — heat on, 147  
   —, — — light on, 147  
   —, — — oxidizing agents on, 150  
   —, — — salts on, 149  
   —, bleaching of, 255  
   —, boiling off, 250  
   —, composition of, 143  
   —, detection of damage to, 148  
   —, gum, 145  
   —, properties of, 144  
   —, structure of, 142  
   —, weighting, 149  
 Silk-wool mixtures, dyeing of, 482  
   — — —, two-colour effects on, 363  
 Skin, structure of, 153  
 Smalt, 332  
 Soap, 193  
   —, detergent action of, 197  
   —, emulsifying power of, 196  
   —, estimation of, in fabrics, 88  
   —, powdered, 202  
   —, preparation of, 194  
   —, properties of, 194  
   —, selection of, for scouring and dyeing, 199 ff.  
   —, sulphonated, 199  
   —, textile, 202  
   —, types of, 201  
   —, for wool scouring, 269  
 Soaps, hard and soft, 193  
   —, residual, in wool, 180  
 Sodium bicarbonate, 209  
   — bisulphite, 219  
   — borate, 209  
   — carbonate, 207  
   — dichromate, 243  
   — hexametaphosphate, 61  
   — hydrosulphite, as reducing and bleaching agent, 219  
   — hydroxide, 207  
   — hypochlorite, preparation of, 224  
   — metabisulphite, 219  
   — peroxide, as oxidizing and bleaching agent, 238  
   — silicate, 209  
   — sulphate, 330  
   — sulphite, as bleaching agent, 218  
   — sulphoxylate formaldehyde, 220  
   — tetraborate, 209  
   — tungstate, 333  
 Softening agents, 330  
 Soft soaps, 193, 202  
 Soledon Jade-green, 458  
 Soxhlet extractor, 265  
 Spectroscope, 488  
 SRA dyestuffs, 475  
 Stains, removal of, 512  
 Stannic chloride, 431  
 Stannous chloride, 430  
 Staple fibre (rayon), 135  
 Starch, 317  
   —, action of acids on, 319  
   —, — — alkalis on, 321  
   —, — — enzymes on, 322  
   —, — — formaldehyde on, 322  
   — mangles, 333-4  
   —, microscopic structure of, 320  
   — paste, thickening of, 321  
   —, preparation of, 317  
   —, properties of, 318  
   —, soluble, 322  
   —, thin, 323  
   —, varieties of, 317, 320  
 Stentering, 335  
 Stiffening agents, 317  
 Streakiness, 511  
 Stripping agents, 360  
 Substantive dyestuffs, 381 (*see* Direct dye-stuffs)  
 Sudan CB, 403  
 Suint, 165  
 Sulphonated oils and soaps, 199  
 Sulphon-cyanines, 359  
 Sulphur dioxide as bleaching agent, 216  
   —, estimation of, 217  
 Sulphur dyestuffs, 409  
   —, after-treatment of, 413  
   —, assistants for, 411  
   —, cotton, application to, 411  
   —, —, tendering effect on, 410  
   —, dissolving, 411  
   —, identification of, 497  
   —, properties of, 410  
   —, standing baths for, 412  
   —, wool and silk, application to, 414  
 Sulphuric acid, 211  
   —, specific gravity data for, 213  
 Sulphurous acid, 217  
 TALC, 329  
 Tallow, 330  
 Tannic acid in cotton, 108  
   —, combines with basic dyes, 372  
   —, mordanting with, 377  
 Tartaric acid, 215  
 Tenderness in dyed goods, 512  
 Tensile strength of yarns, tests of, 80  
 Tetralin, 249  
 Textile fibres, analysis of, 129  
   —, artificial, 215  
   —, classification of, 64  
   —, general properties of, 63  
   —, special tests for, 65  
   — materials, analysis of, 87  
   — yarns, determination of condition weight of, 72  
   —, — — count of, 74  
   —, — — tensile strength of, 81  
   —, — — twist of, 85  
 Thio-indigos, 453  
 Tin chlorides, use of, in logwood dyeing, 430-31



- Tin phosphates, 432  
 — silicates, 432  
 Tintometer, 493  
 Titanous chloride, titration of dyestuffs with, 506  
 Titration of dyestuffs, 505  
 Toluylene Red, 370  
 Topping with basic dyes, 388, 396  
 Turkey Red oil, properties and uses of, 199  
 — — on cotton, 440  
 Tussur silk, 151  
 Twist of yarn, measurement of, 85
- ULTRAMARINE**, 332  
 Uneven colours, 358, 360, 511
- VAT** dyestuffs, 448  
 — —, anthraquinone, 453  
 — —, application of, 455  
 — —, detection of, 459  
 — —, fastness of, 457  
 — —, estimation of, on textile fabrics, 459  
 — —, identification of, 497  
 Victoria Blue, 369, 376, 500  
 Vidal Black, 409, 415  
 Vinyon, 527  
 Viscose rayon, 133  
 — —, bleaching of, 464  
 — —, dyeing of, 464  
 — —, — —, in mixtures, 485  
 — —, uneven dyeing, correction of, 468  
 Vulcan colours, 388
- WATER**, 47  
 —, corrosive, nature of, 51  
 —, dissolved impurities in, 49  
 —, foaming, 53  
 —, hardness in, 49  
 —, — —, method of expressing, 50  
 —, scale-forming, 51  
 —, softening, 53  
 —, softeners, 55  
 —, treatment of organic matter in, 62
- Waterproofing, 191  
 Waxes, 190  
 Wear-testers for fabrics, 86  
 Wetting agents, 203  
 Woaded blacks, 427  
 Wool, 153 ff.  
 —, abnormal fibres, 163  
 —, action of acids on, 176  
 —, — — air on, 171  
 —, — — bleaching agents on, 181  
 —, — — chlorine on, 181  
 —, — — formaldehyde on, 181  
 —, — — heat and light on, 175  
 —, — — micro-organisms on, 181  
 —, — — salts on, 180  
 —, — — soap on, 179  
 —, bleaching with hydrogen peroxide, 278  
 —, — — permanganate, 278  
 —, — — sodium peroxide, 278  
 —, — — sulphur dioxide, 276  
 —, bromination of, 185  
 —, carbonization of, 177  
 —, characteristics of, 161  
 —, chlorination of, 181  
 —, chlorinated, tests for, 187  
 —, classification of, 162  
 —, composition of, 165  
 —, detection of damage to, 173  
 — fat, 165  
 —, felting of, 161, 170  
 —, properties of, 168  
 —, raw, 165  
 —, scouring of, 262  
 —, staple, 161  
 —, unshrinkable finishes, 527  
 Woollen goods, finishing of, 279  
 Wrap reel, 75
- XANTHATES**, 133
- YEASTS**, 35
- ZINC** chloride, 332





